Interpretation of results from Quantemol-EC

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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.

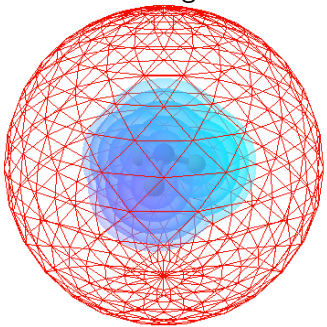
Introduction to QEC

- 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.

inner region



outer region

connection to asymptotic forms

Single outgoing electron

Exchange, correlation with inner electrons neglected

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

R-matrix theory: inner region

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

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

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

R-matrix theory: outer region

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

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

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

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

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

Scattering models: Static exchange (SE)

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- 1-state target representation (single Φ^N)

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

- χ_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.

Scattering models:Static exchange+polarization(SEP)

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- 1-state target representation

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

- χ_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

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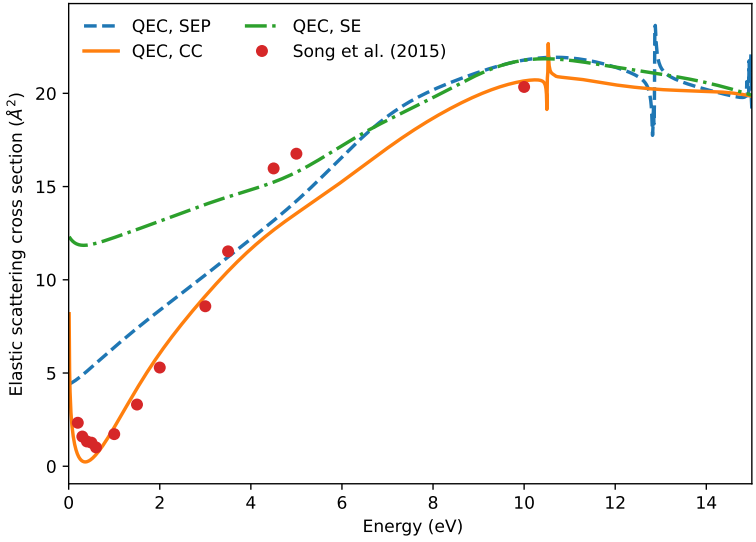
- multi-state target representation (set of Φ_i^N).

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

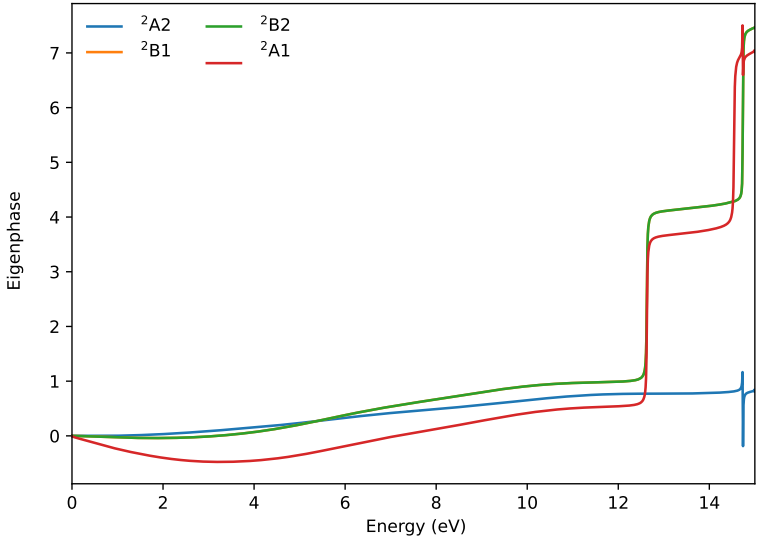
- Complete active space for χ_m^{N+1}.
- Shape and Feshbach resonances can be found.
- Applicable at energies up to first missing excitation threshold.

Results: Elastic scattering cross section CH_4

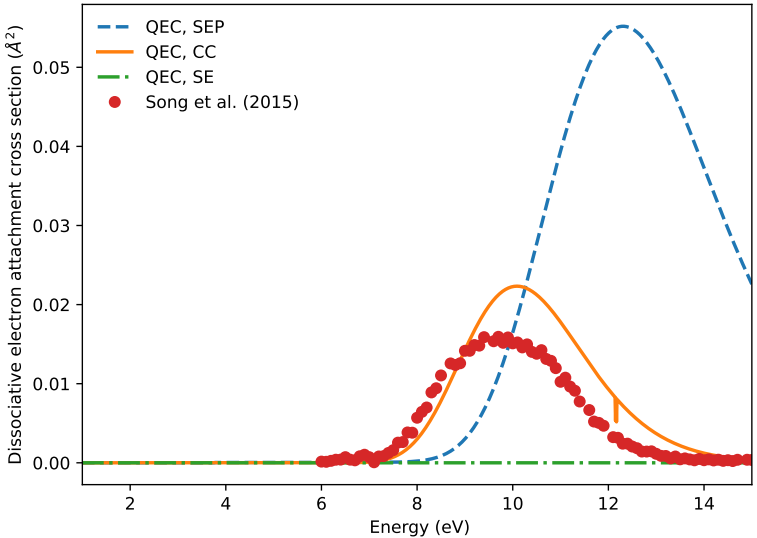


M.-Y. Song et al., J. Phys. Chem. Ref. Data **44** 023101 (2015).

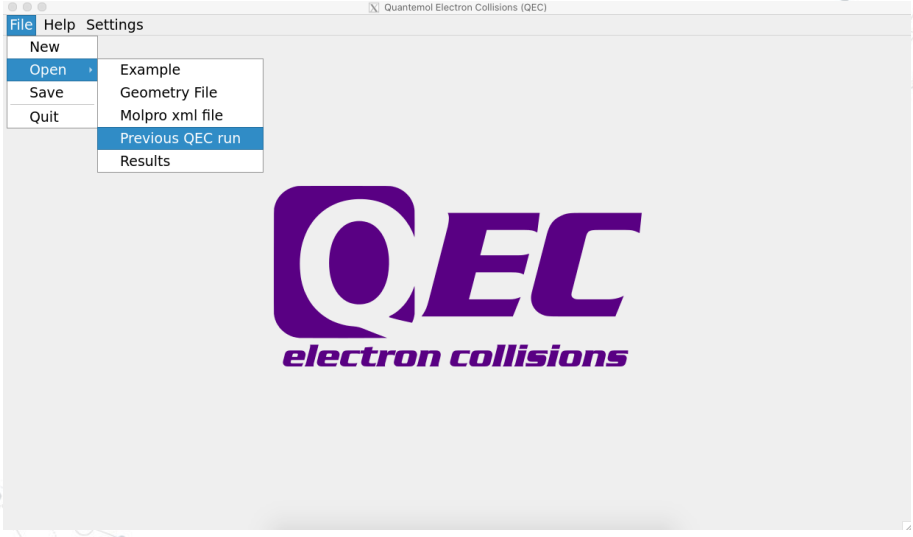
Results: Eigenphases CH_4



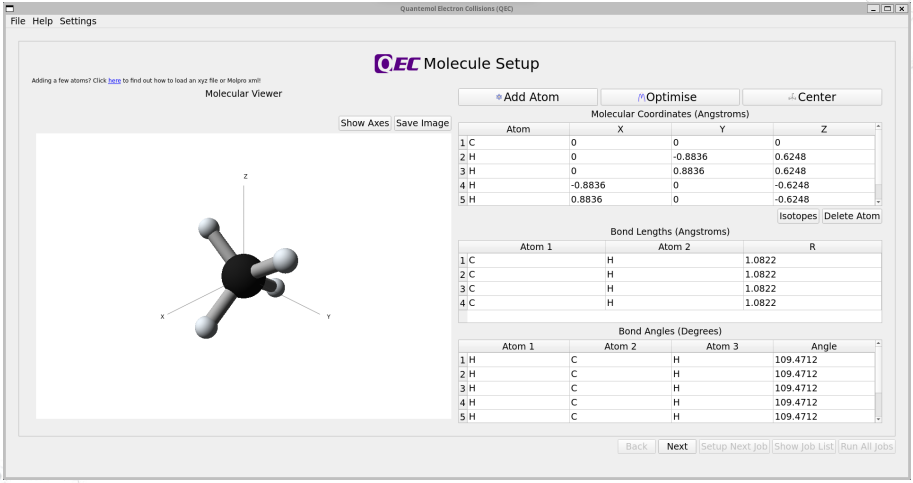
Results: Dissociative electron attachment cross section $e^- + CH_4 \rightarrow CH_3 + H^-$



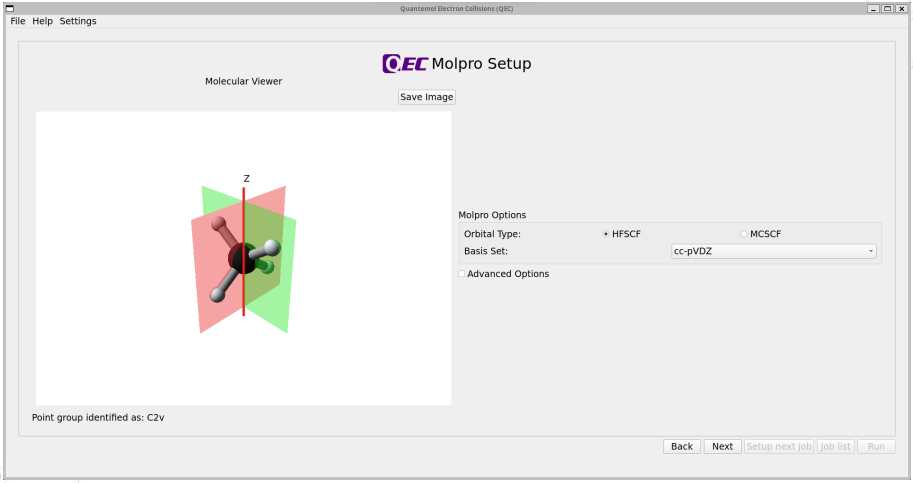
QEC Initial Setup



QEC Molecule Setup



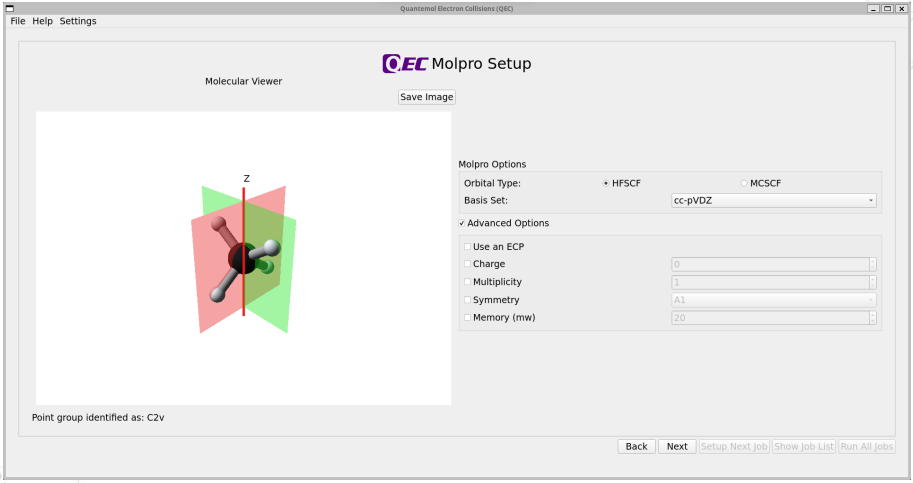
QEC Molpro basis sets and orbitals setup



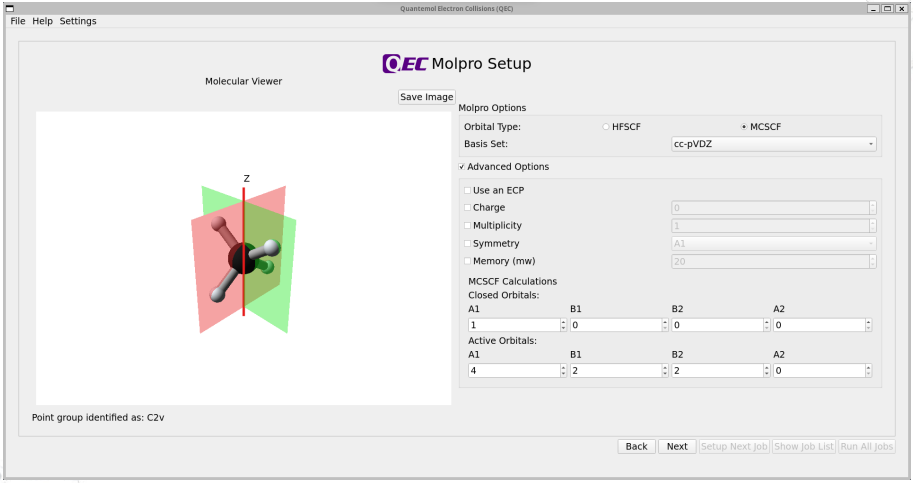
QEC Molpro basis and orbital sets setup

- 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.

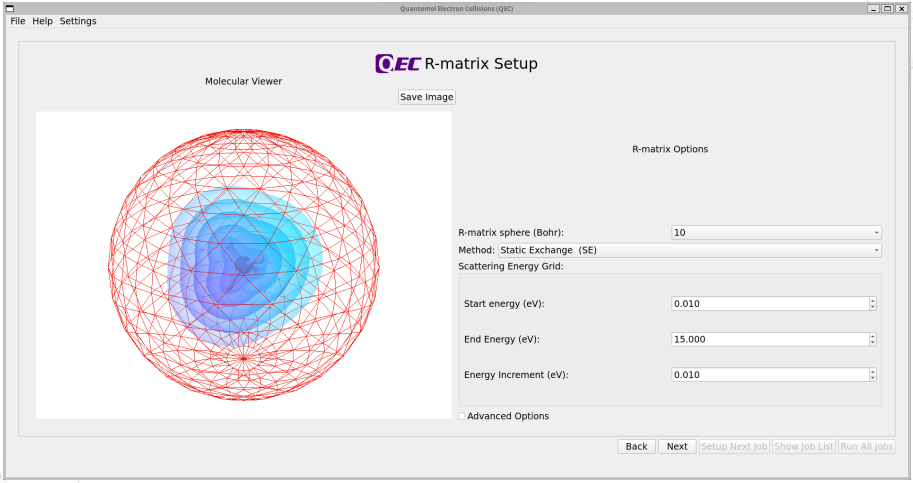
Advanced options for ions, radicals, large systems



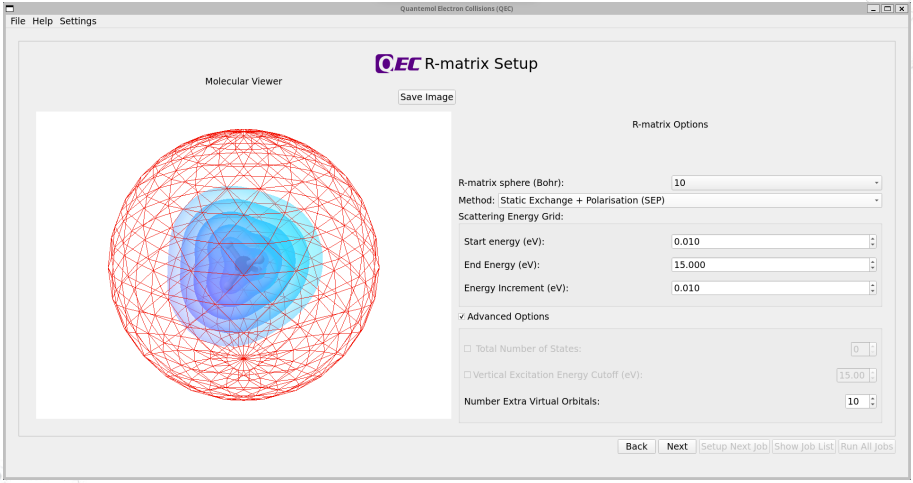
QEC active space (CAS) settings



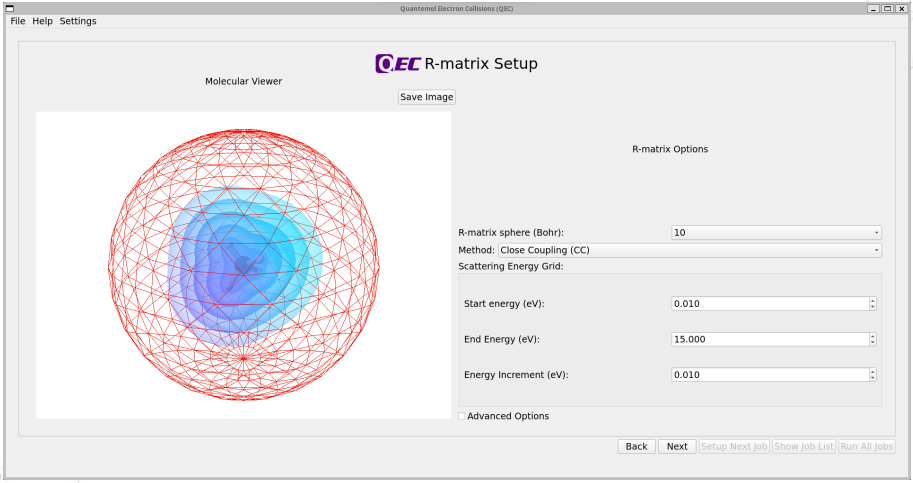
QEC R-matrix setup (SE)



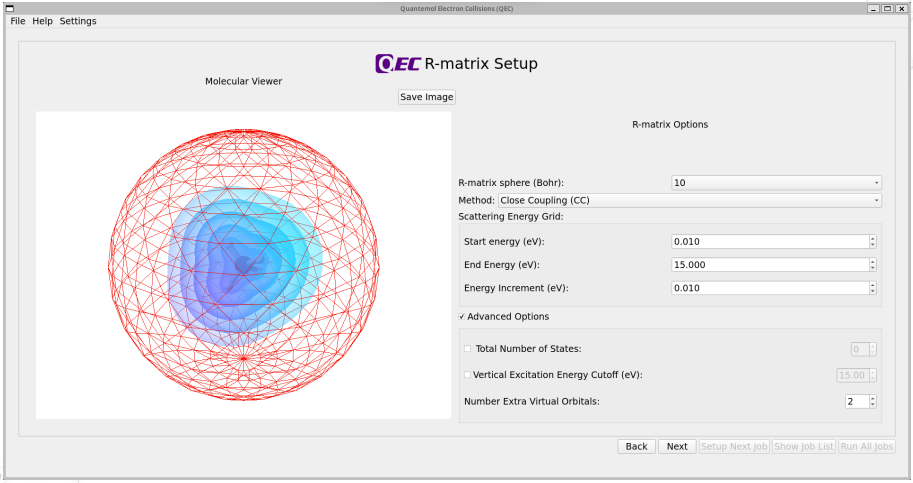
QEC R-matrix setup (SEP)



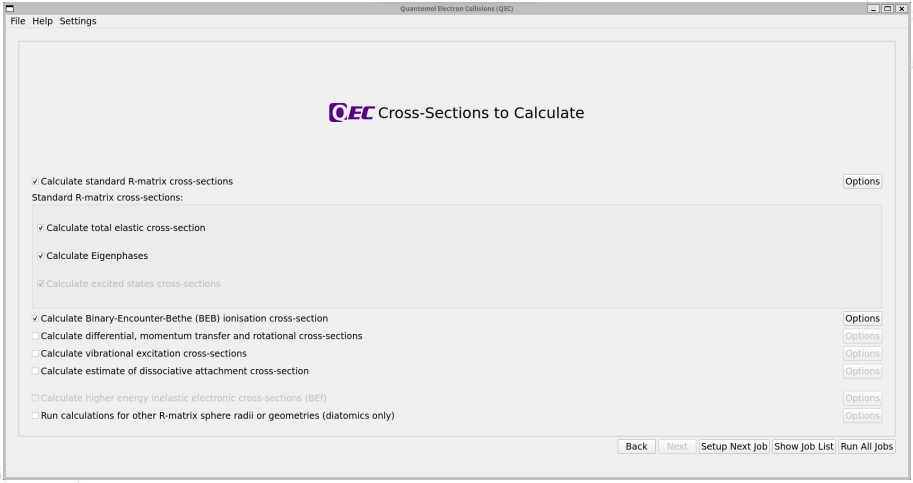
QEC R-matrix setup (CC)



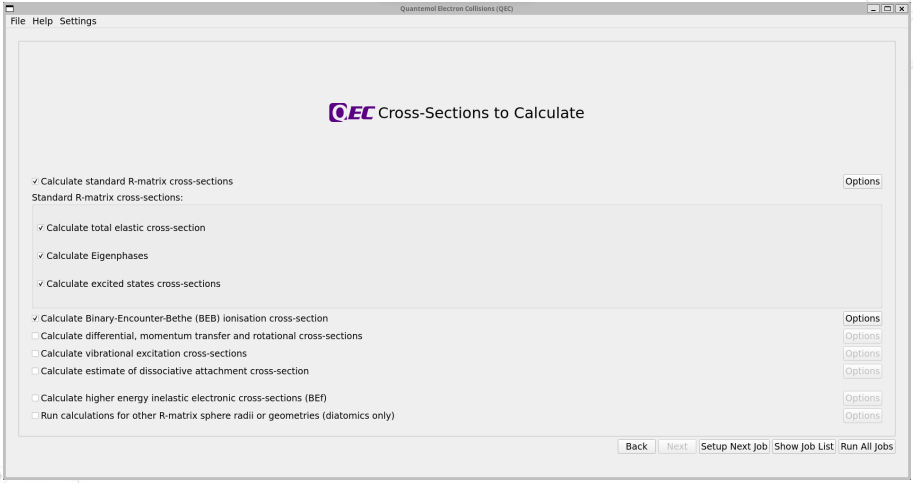
QEC R-matrix setup (CC)



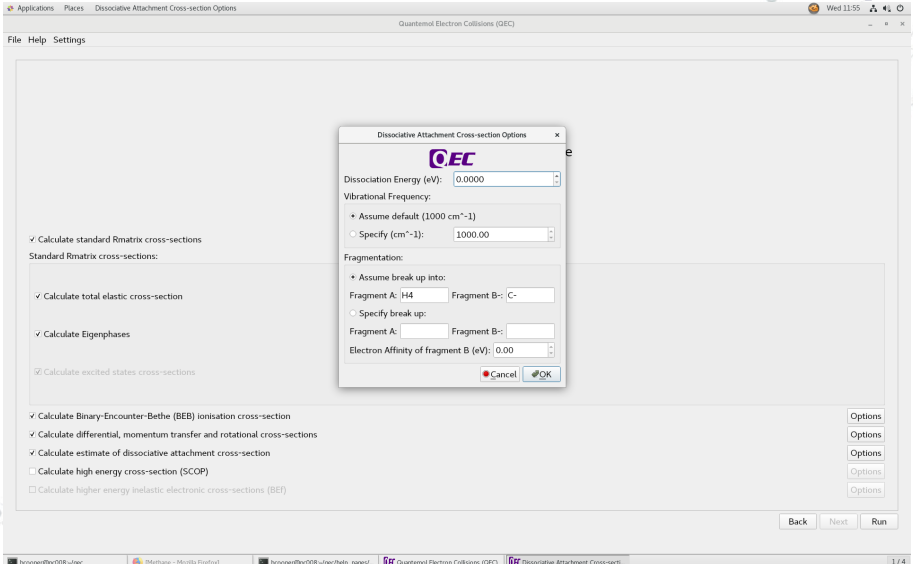
QEC cross sections to calculate (SE or SEP)



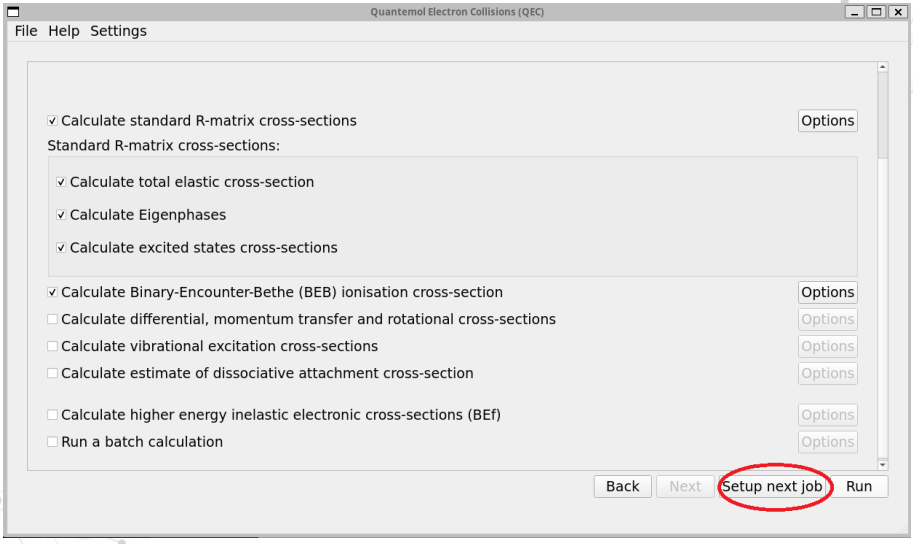
QEC cross sections to calculate (CC)



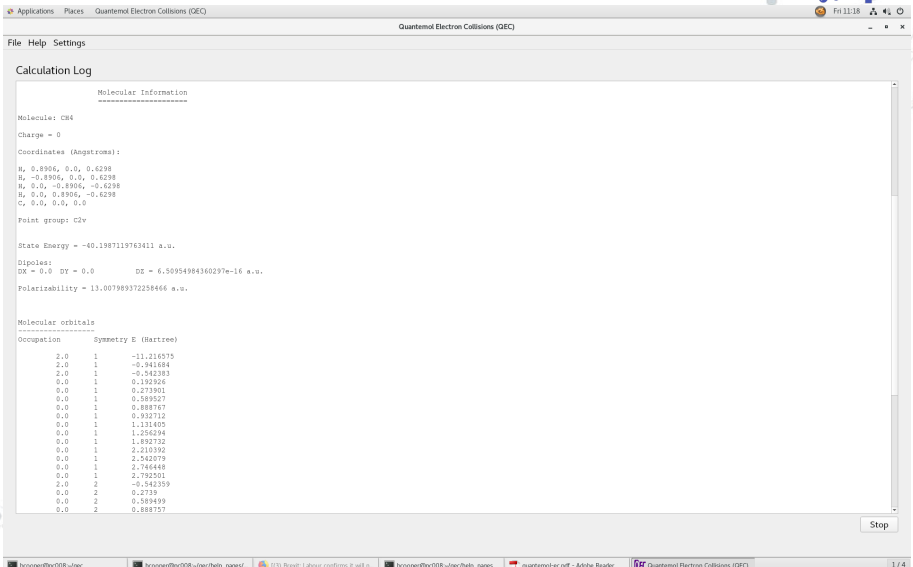
QEC cross sections to calculate (CC)



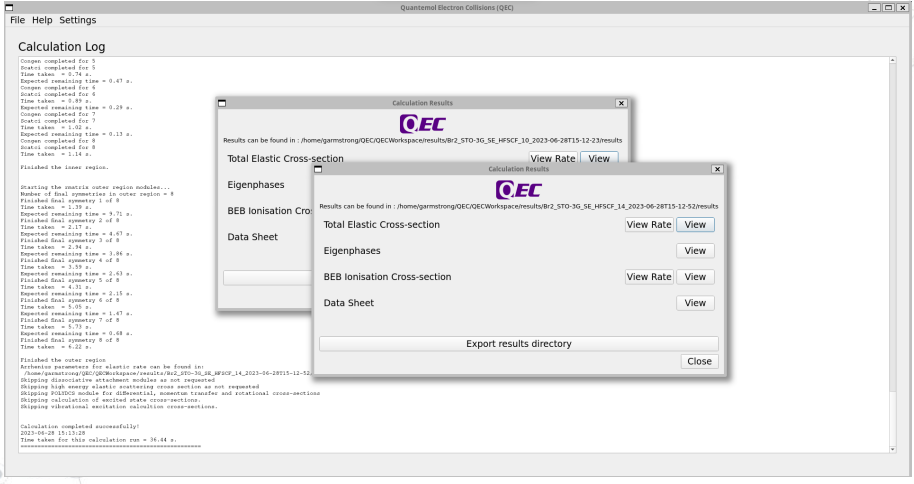
QEC cross sections to calculate (CC)



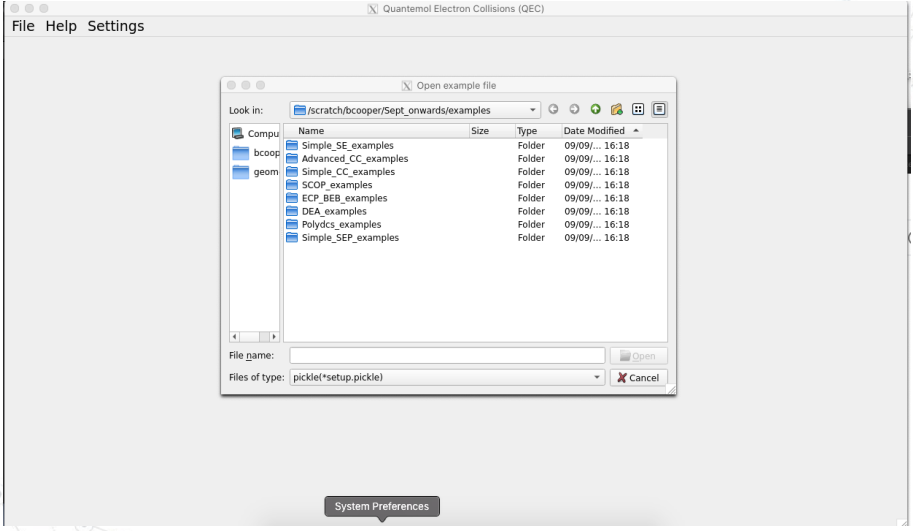
QEC results output



QEC results output



QEC example calculations



Acknowledgements

- Harin Ambalampitiya
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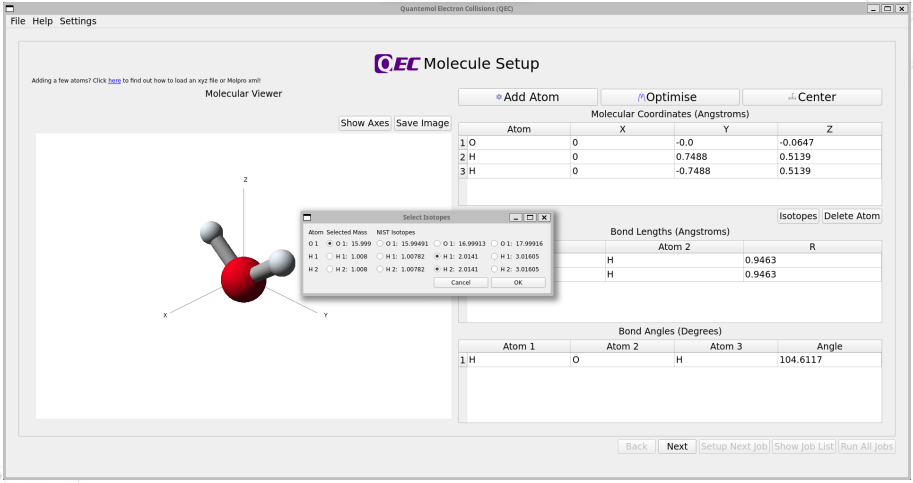
- Sam Giltrap
- Anna Nelson
- Jonathan Tennyson

QEC isotope selection



Isotope selection

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- 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 ArH^+

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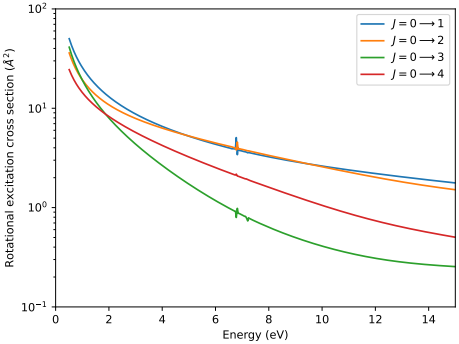
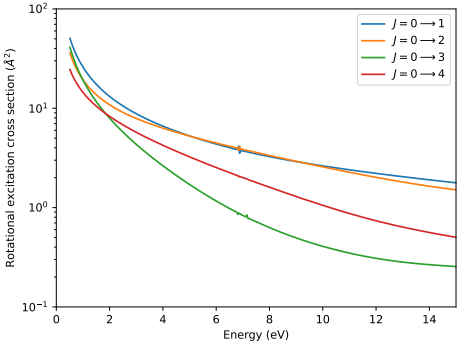
ArH^+ dipole moments		
$^{36}ArH^+$	$^{38}ArH^+$	$^{40}ArH^+$
2.2233	2.2319	2.240

$^{36}ArH^+$



$^{40}ArH^+$



MOLPRO basis sets for heavy elements

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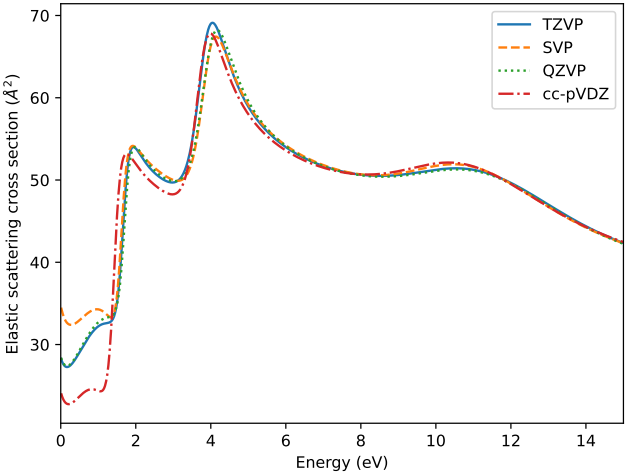
- Heavy: molecules containing elements Ar-Kr.
- Consider all-electron basis sets without core potentials.
- Dunning (cc-pVXZ) and Pople (X-YZWG) basis sets are commonly used.
- Pople basis sets only available for H-Ar.
- Include Karlsruhe bases in QEC for elements Ar-Kr.

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 $GeCl_4$



Rotational excitation cross section for $GeCl_4$

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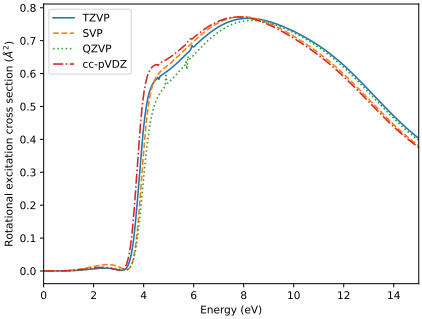
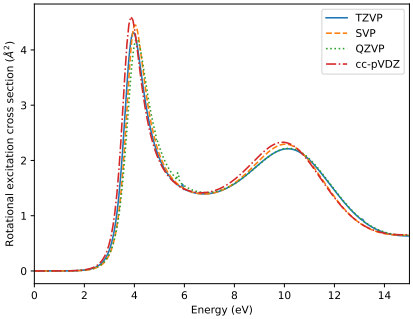
$J = 0 \longrightarrow 1$



$J = 0 \longrightarrow 2$



Vibrational frequencies for $GeCl_4$

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$GeCl_4$				
NIST	cc-p		def2-	
(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