Calculated low-energy electron-molecule collisions for plasma problems

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The R-matrix method

Dominant interactions

Inner region

Exchange
Correlation

\{ Adapt quantum chemistry codes \\
High $\ell$ 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
Two methods of doing R-matrix calculations:

**A. The UK Molecular R-Matrix Codes**

- Freely available online
- People can join as users on CCPForge
- Comprehensive but hard to use
  (Can take a whole PhD (3 years) to correctly run one molecule!)

**B. Quantemol-N**

- Easy to use graphical interface
- Very simple input, requires little scientific knowledge or training
- Extra features (ionisation, dissociative attachment estimator, high energy electronic excitation, etc)

Note also:

**Quantemol-P** 0D plasma chemistry code (runs GLOBAKIN)

**Quantemol-D** 2.5D simulation of industrial plasma processessing (runs HPEM)
UKRMol inputs: electron – silane (SiH₄)
Quantemol-N inputs:
electron – silane

Si – H bondlength
Main advantages of using Quantemol-N:

- User friendly interface, which vastly simplifies setting up an R-matrix simulation.
- Full tutorial system to reduce learning curve.
- Library containing 40+ examples.
- Easy to use results format.
- 24/7 service support from Quantemol team.
Quantemol-N 4.1 can calculate:

- Elastic cross-sections
- Electronic excitation cross-sections (extended to high energies with BEf)
- Super-elastic cross-sections between excited states
- Electron impact dissociation
- Scattering reaction rates
- Resonance parameters
- Dissociative electron attachment cross-sections estimator
- Differential cross-sections
- Momentum transfer cross-sections
- Atomic cross-sections
- Electron impact ionisation at all energies (BEB)

Red: features not in standard code
Examples obtained using Quantemol-N
Chlorine – Dissociative Attachment

- DZP basis for the target and frozen bond-length of 1.988 Angstrom.
- CAS-CI representation: 20 core electrons are frozen (Cl 1s, 2s and 2p orbitals).
  - 14 active electrons are distributed as: (4 - 6σ_g, 4 - 5σ_u, 2π_u, 2π_g)^14.
- Lowest virtual orbitals of σ_g, σ_u and π_u retained in the scattering calculation.

48 target states in the close-coupling expansion.

Dissociative electron attachment cross sections for Cl₂
Calculations used the DEA cross section estimator in Quantemol-N
Oxygen – Dissociative Attachment

- Calculations: 6-311G* target basis at frozen bond length of 1.2144 Å.
- Target CAS: 4 core electrons frozen, and 10 electrons in 12 valence orbitals:
  \((1\sigma_g, 1\sigma_u)^4 (2\sigma_g, 3\sigma_g, 2\sigma_u, 3\sigma_u, 1\pi_u, 2\pi_u, 1\pi_g)^{12}\).
- Scattering calculation augmented with the \(4\sigma_g\), \(4\sigma_u\), and \(2\pi_g\) orbitals. 48 states retained in close-coupling expansion.
RLSA (Radial Line Slot Antenna) micro-wave plasma reactor

1. Micro-wave excited a high density plasma.
2. Plasma is transported by diffusion, Te is cooled and uniformed.
3. RF bias works only accelerating ion, not for plasma generation.
Why does High Press. Process make vertical profile? 

**Pressure dependency**

- **HBr/Ar Process**
- **Vpp : Const. = 415V**
- **Residence time : Const. = It is proportional to Pressure**

<table>
<thead>
<tr>
<th>Press. (mT)</th>
<th>40</th>
<th>70</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RF (W)</strong></td>
<td>113</td>
<td>80</td>
<td>73</td>
<td>70</td>
</tr>
<tr>
<td><strong>Etch.D.</strong></td>
<td>232(147%) / 158</td>
<td>205(144%) / 142</td>
<td>204(121%) / 168</td>
<td>216(108%) / 200</td>
</tr>
<tr>
<td><strong>Taper</strong></td>
<td>81• / 68•</td>
<td>86• / 81•</td>
<td>86• / 84•</td>
<td>86 / 85•</td>
</tr>
</tbody>
</table>

The higher pressure, The Dense/Iso pattern dependence is getting better.
Reaction model

- Charged species: $e^-$, Br$^-$, Ar$^+$, HBr$^+$, Br$^+$, Br$_2^+$, SiBr$_2^+$, and SiBr$^+$
- Neutral species: Ar, Ar*, HBr, Br, Br$_2$, H$_2$, H, SiBr$_2$, SiBr, and SiBr$_2$
- Electron impact reactions: Ionization, excitation, dissociation, attachment, and recombination
- Ion – neutral reactions
- Ion – ion reactions
- Molecule – molecule reactions
  
  SiBr, SiBr$_2$, SiBr$^+$, SiBr$_2^+$ omitted in original chemistry
$\text{Ar/Cl}_2 = 90/10 \text{ sccm}$
$500 \text{ W ICP}$
$15 \text{ mTorr}$

“Re-flux” of SiCl$_2^+$ was important but was not dominant at this lower pressure.

Agarwal A. & Kushner M.
JVSTA 26 (2008) 498
- Study effect of etching by-products (SiBr$_x$) on the plasma.
- Quantemol-N estimates of cross sections for new species.
- Below estimated dissociative electron attachment cross sections for SiBr and SiBr$_2$.
- Full cross section set calculated for these species.

Estimated DAE cross sections as a function of electron impact energy.
Number is maximum [#/cm³]

With \( \text{SiBr}_x \) reactions

Electron distributions are localized near top, because microwave heat comes from top.

Br negative ion produced both inlet and near wafer because of attachment reaction of \( \text{SiBr}_x \).

\( \text{SiBr}_2 \) in case with \( \text{SiBr}_x \) reactions is localized near wafer because there are reactions of \( \text{SiBr}_2 \).
SiBr and Si are produced from SiBr$_2$ and SiBr respectively.

Ions produced from byproducts are localized near wafer which is dominant ions attack to wafer.
Ion fluxes on wafer

Without SiBrx reactions

Including SiBrx reactions
- Ion mass gets heavier as pressure increases
- Ion fluxes and energies will change significantly with pressure in this collisional sheath.
Re-entry physics: plasmas created on spacecraft (rocket) re-entry

Vibrational excitation of key molecule: Venus, Mars, Earth
Electron – CO: $^2\Pi$ resonance

R-matrix resonance positions and widths

Static exchange plus polarisation (SEP) model
Electron - CO: resonance enhanced vibrational excitation $0 \rightarrow v'$
Electron – CO: resonance enhanced vibrational excitation

High $v' - v''(>0)$

V Laporte, CM Cassidy, J Tennyson & R Celliberto,
Plasma Sources Science and Technology (to be submitted)
Conclusions:

R-matrix method powerful for generating plasma data

- Quantemol-N expert system simplify use of the fully quantum mechanical R-matrix codes electron-molecule cross-sections

- Quantemol-N calculates cross-sections for species which are difficult to study experimentally (e.g., radicals)

  - Results can be (are being) used to improve the simulation of complex (technological) plasmas
Memorial to the Japanese pioneers who came to UCL in 1863 and 1865

www.quantemol.com
Conclusions: electrons collisions with RMPS method

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. C₂⁻)

- Also **greatly** improves treatment of positron-molecule collisions
- **Computationally very expensive**
R-matrix method for electrons: inner region wavefunction

(within the Fixed-Nuclei approximation)

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

\( \phi_i^N = \text{target states} = \text{CI target built from nuclear centred GTOs} \)

\( \phi_j^{N+1} = L^2 \text{ functions} \)

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

\( A = \text{Anti-symmetriser} \)

\( a_{i,j,k} \text{ and } b_{j,k} \text{ variationally determined coefficients} \)
Target Wavefunctions

\[ \phi_i^N = \sum_{i,j} c_{i,j} \zeta_j \]

where

- \( \phi_i^N \) N-electron wavefunction of \( i^{th} \) target state
- \( \zeta_j \) N-electron configuration state function (CSF) Usually defined using as CAS-CI model.
- \( c_{i,j} \) variationally determined coefficients
The R-Matrix Method

- The sphere, of radius $a$, has the centre of mass of the molecule as its origin;
- the sphere contains the electron cloud of the molecule;
- equations of motion are solved in the body-fixed frame (fixed nuclei approximation)

The **Trial** Scattering Wavefunction

\[
\psi_k = \sum_{i,j} a_{ijk} \varphi_i \eta_{ij} \sum_k b_{ik} \chi_k
\]

**Target wavefunction** - obtained by methods of Quantum Chemistry, represented by GTOs centred on atomic nuclei

**Continuum wavefunction** - representing the scattering electron, represented by GTOs on *centre of mass*

**Correlation functions** - accounts for when the scattering electron occupies a target orbital

**Expansion coefficients** obtained by variational methods (matrix diagonalisation).

**Antisymmetriser** to represent exchange (Pauli Principle)
Improving on SEP and close-coupling

Use Pseudostates to approximate second continuum. Good for

- Impact ionisation
- Extending calculations to intermediate energy
- Representing target polarization
- $e^- - e^+$ correlation and annihilation
Intermediate impact energies

Ionization

\[ AB + e \rightarrow AB^+ + e + e \]

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 (BEB, DM, etc.): 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 \( \phi_i^N \) 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
Pseudostates

- represent ionized state
  \[ \Rightarrow \text{can’t expand in} \]
  bound target state orbitals

- contained inside the box

\[
\text{PCO: orbitals representing ionized electron: } \sum \text{GTOs centred at CM}
\]

Even-tempered GTO exponents \( \alpha_i = \alpha_0 \beta^{(i-1)} \)

choice of \( \alpha_0 \) and \( \beta \) allows systematic generation of basis for PCOs

**Care must be taken to avoid linear dependence!!**
R-matrix with pseudostates (RMPS) method

Reality

Continuum

RMPS

Ionization threshold

Ground state $E = 0$

Li$_2$: RMPS
Target states

Ground state $E = 0$
Example: $\text{H}_3^+$

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

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

- Kohn calculation: Orel (1992)

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 $\text{H}_3^+$

Electronic excitation of $\text{H}_3^+$

Quantum defect for resonances increased by about 0.05
R-matrix with Pseudostates Method (RMPS)

Polarizability of H$_3^+$ (in a.u.)

<table>
<thead>
<tr>
<th>States in close-coupling expansion</th>
<th>$\alpha_{\text{parallel}}$</th>
<th>$\alpha_{\text{perpendicular}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (physical target states)</td>
<td>-3.2848</td>
<td>-0.0638</td>
</tr>
<tr>
<td>28 ($E_{\text{cut}}=33.47$ eV)</td>
<td>-3.4563</td>
<td>-2.0893</td>
</tr>
<tr>
<td>64 ($E_{\text{cut}}=45$ eV)</td>
<td>-3.5247</td>
<td>-2.2093</td>
</tr>
<tr>
<td>152 ($E_{\text{cut}}=132$ eV)</td>
<td>-3.5336</td>
<td>-2.2480</td>
</tr>
<tr>
<td>Accurate ab initio value</td>
<td>-3.5978</td>
<td>-2.2454</td>
</tr>
</tbody>
</table>
Mean polarizability of H$_2$O (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


Needs

- Electron collisions from an anion
- Molecular R-Matrix with PseudoStates (MRMPS)
- Partitioned R-Matrix method
Electron – anion ($C_2^-$) scattering
Models with Pseudostates

Target model:
\[ \text{targ}^N \]
\[ \text{targ}^{N-1} \text{ PCO}^1 \]

Scattering model:
\[ \text{targ}^N \text{ CO}^1 \]
\[ \text{targ}^{N-1} \text{ PCO}^1 \text{ CO}^1 \]
\[ \text{targ}^{N+1} \]
\[ \text{targ}^N \text{ virtual}^1 \]
\[ \text{targ}^{N-1} \text{ virtual}^2 \]
\[ \text{targ}^{N-1} \text{ PCO}^2 \]
\[ \text{targ}^{N-1} \text{ PCO}^1 \text{ virtual}^1 \]

\( \text{target} \times \text{continuum} \)
\( \text{L}^2 \text{ configuration} \)

\( \text{targ} = \text{target molecular orbitals} \)
\( \text{PCO} = \text{pseudo continuum orbital} \)
\( \text{CO} = \text{continuum orbital} \)
\( \text{virtual} = \text{unoccupied target orbital} \)
MRMPS, partitioned R-matrix calculation for electron - C$_2^-$

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

Electron impact ionisation: $\alpha = 0.17$
Electron impact ionisation: $\alpha = 0.15$
Electron impact ionisation: several $\alpha$’s
C$_2^{2-}$ resonances

Find 3 broad resonances for

\[
\begin{array}{ccc}
\text{E/eV} & \text{Γ/eV} \\
^{1}\Sigma_{g}^{+} & 4.86 & 0.65 \\
^{3}\Pi_{g} & 9.71 & 1.14 \\
^{1}\Pi_{g} & 10.92 & 0.52 \\
\end{array}
\]

(also predicted by Sommerfeld et al (2000))

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

How common is this type of resonance?
Positron collisions?
Cross sections?

- Use of $l < 5$ does not give background cross section
- Coulomb potential long range so high $l$’s important
- Dipole-Born approximation to give transitions to the continuum