MOLECULAR PROCESSES II

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Electronic resonances

**Shape resonance: 1 particle**

- Target in an excited state
- Multi-electronic description essential
- Harder to observe (particularly Feshbach): EELS experiments
- Longer-lived

**Core-excited: 2-particle, 1 hole**

- Target in electronic ground state
- Can be modelled as a single-electron problem
- Visible in ETS experiments
- Short-lived

**Metastable state where the electron is temporarily captured by target**

- Target in an excited state
- Multi-electronic description essential
- Shape or Feshbach
- Harder to observe (particularly Feshbach): EELS experiments
- Longer-lived
Resonances

Metastable state where the electron is temporarily captured by target. Decay by autoionization: energy and width (lifetime) or dissociative electron attachment.

DEA: resonant process initiated by formation of a resonance:

\[
AB + e \rightarrow (AB)^* \rightarrow A^- + B \rightarrow A + B^-
\]
Resonance effect on scattering


Applied relevance

Nanofabrication

Plasmas in medicine

Scientific Reports 6 (2016) 34003

Chapman, Lawrence Livermore National Laboratory

Osaka University

W. Friedland, GSF-Institute of Radiation Protection. PARTRAC, MC simulation
Low energy $e^-$ scattering calculations

- Quantum mechanical approach needed
- Time-independent approaches developed and implemented computationally for over 40+ years
- Electron in the continuum means bound state Quantum Chemistry methods are not valid
- Electronic transitions are treated in the fixed-nuclei approximation
- To treat rotational excitation: adiabatic nuclei rotation approximation
- To treat vibrational excitation: AN, Discrete Momentum Representation, etc.
Computational machinery

• Electronic scattering approaches:
  • R-matrix (UK, Czech Republic, India, etc.)
  • Schwinger multichannel (Brazil, USA)
  • Kohn variational method (USA)
  • Single-centre approaches (Italy, Poland)
  • Convergent Close-Coupling (Australia)

- In addition, to identify and characterize resonance, methods adapted from Quantum Chemistry: CAP, stabilization techniques, analytical continuation,....
Low energy electron-molecule scattering

Time-independent approaches developed and implemented computationally over 40+ years

\[(H_{N+1} - E)\Psi_E(x, \gamma) = 0\]

\[H_{N+1} = H_N(x) + \hat{T}_e(\gamma) + \hat{V}_{\text{int}}(x, \gamma)\]

subject to the appropriate boundary conditions

- Main issues: description of continuum and electron correlation
- Polarization is also an important effect, especially if target is non-polar
Exchange and correlation

- **Exchange** arises due to electrons being indistinguishable particles.
- Indistinguishability must be taken into account when wavefunctions are built.
- Electrons are fermions and must obey Fermi-Dirac statistics. (For bound electrons in atoms and molecules this translates into the Pauli Exclusion principle)
- Exchange integrals describing exchange interaction (with no classical equivalent) arise

- **Correlation** is due to the interaction of N moving charged particles, the electrons.
- Can be seen as the effect of the instantaneous repulsion felt by one electron due to all others.
- Can be difficult to model accurately for electron-rich molecules
Molecular R-matrix method

**Fixed-Nuclei approximation** but use of other software to treat nuclear motion

- exchange and correlation important
- Explicitly multielectronic
- Basis set methods
- Multicentre expansion

**Outer region:**
- exchange and correlation are negligible
- One explicit electron
- single centre expansion
- long-range multipolar interactions

**R-matrix sphere (box) of radius** $a$

Describing electronic target states

Use computational chemistry approaches

\[ \Phi_i^N = \sum_{i,j} c_{i,j} \zeta_i^N_j \]

\[ \zeta_i^N_j = \text{N-electron configuration state function (CSF)} \]
\[ = \| \varphi_1 \varphi_2 \varphi_3 \ldots \varphi_N \| \]

\[ \varphi_i = \text{molecular orbitals} \]

\[ C_{i,j} = \text{variationally determined coefficients} \]
Molecular R-matrix method

**Inner region:** close-coupling expansion

\[ \psi_k^{N+1} = A \sum_{i,j} a_{i,j,k} \Phi_i^N \eta_{i,j} + \sum_j b_{j,k} \phi_j^{N+1} \]

Choice of **continuum orbital** \( \eta_{i,j} \), \( L^2 \) functions \( \phi_j^{N+1} \) and target states \( \Phi_i^N \)
defines the quality of the calculation and model.

Coefficients \( a_{i,j,k} \) and \( b_{j,k} \) obtained variationally.

- **Static-Exchange (SE):** \( \Phi_i^N \) (HF ground state) + FEW \( L^2 \) functions
- **Static-Exchange plus Polarization (SEP):** \( \Phi_i^N \) (HF ground state) + \( L^2 \) functions
- **Close-Coupling (CC):** \( \Phi_i^N \) \((i=1,2,3,\ldots)\) + \( L^2 \) functions
Molecular R-matrix method

**Outer region:**

\[
F_i(r) = 2 \sum_j V_{ij}(r) F_j(r)
\]

with inner region data providing initial conditions via R-matrix

\[
w_{pk}(a) = \frac{1}{\sqrt{2}} \left( \phi_{p}^{r} \frac{1}{r} \psi_{k}^{N+1} \right)_{r=a} = \frac{1}{\sqrt{2}} \left( \phi_{p}^{r} \frac{1}{r} X_{l_p,m_p}(\hat{r}) \psi_{k}^{N+1} \right)_{r=a}
\]

At \( r > 50-100 \) \( a_0 \) K-matrices obtained

\[
F_{ij} \sim \frac{1}{\sqrt{k_i}} \left( (\sin(k_ir - \frac{1}{2}l_i\pi) \delta_{ij} + \cos(k_ir - \frac{1}{2}l_i\pi) K_{ij} \right)
\]

\[
S = (1 + iK)(1 - iK)^{-1}
\]

\[
T = S - 1
\]

\[
\sigma(i \rightarrow i') = \frac{\pi}{k_i^2} \sum_{s} \frac{(2S + 1)}{(2S_i + 1)_{\Gamma l'}} \left| T_{i\Gamma\Gamma l'} \right|^2
\]
UKRmol+ suite

Source code: https://zenodo.org/ (cmake files and test suite included)

arxiv.org/abs/1908.03018
UKRmol+ suite

Electron scattering: $e^- + H_2 \rightarrow H_2 + e^-$

Positron scattering: $e^+ + H_2 \rightarrow H_2 + e^+$

Photoionization: $H_2 + h\nu \rightarrow H_2^+ + e^-$

- **Positron**-molecule collisions (excluding Ps formation)
- **Photoionization** of molecules
- Input for R-matrix with time approach that solves TDSE to model strong-field processes

**UKRmol-scripts**: A Perl-based system for the automated operation of the photoionization and electron/positron scattering suite UKRmol+

Houfek et al, CPC, **298**, 109113 (2024)

https://doi.org/10.1016/j.cpc.2024.109113
UKRmol+ suite

- Initial code for electron-diatom molecules (early 80s). Polyatomics: mid-90s. Parallelization and modernization early-00s. Overhaul of most of the programs 2010s: UKRmol+ a interfacing with time-dependent R-matrix with time (RMT) codes for strong-field processes. Multiphoton ionization...

Capabilities:
- 2000: electronic excitation of $\text{H}_2\text{O}$:10 e⁻, 9 electronic states, 60 channels (per symmetry)
- 2014: $\text{CH}_4 > 1000$ channels (Brigg et al JPB)
- 2016: electronic excitation of $\text{pBQ}$, 56 e⁻ (Loupas PCCP); 2017: elastic scattering from thymine-$\text{(H}_2\text{O})_5$. > 100 e⁻ (Sieradzka JCP)
- 2020: $\text{H}_2$, $a = 100$ a₀ (Meltzer et al JPB). Excellent agreement with CCC.

In practice:
- < 1 hour on a desktop computer for elastic scattering for mid-size molecules
- > days on a supercomputer for electronic excitation of molecules with 40+ electrons
- Finding appropriate model can take some effort!
Inelastic cross sections $\text{BeH}_2$

Present in plasma in divertors of thermonuclear fusion reactors (e.g. ITER)

State-to-state integral and DCS for electron excitation
Expected behaviour for singlets and triplet states
Radiobiological damage

Ionizing radiation

(Adapted from M. Folkard)

2 μm

Thymine
Cytosine
Uracil

Pyrimidine

Sugar-phosphate backbone

Bases

Hydrogen bonds between bases
Elastic scattering from pyrazine

Elastic DCS


Elastic cross sections in good agreement if polarizability well described

Integral elastic cross section
EELS: Pyrimidine

EELS: measurement of **absolute** electronic excitation cross sections using relative flow technique and accurate calculated cross sections for He.

Representative EEL spectra

State overlap implies EEL measurements for **bands** not individual states.

Regeta et al, JCP 144 (2016)
Electronic excitation of Pyrimidine

- Quantitative inelastic cross sections
- 7 core-excited shape resonances confirmed

Regeta et al, JCP 144 (2016)
Rotational excitation

- Adiabatic nuclei rotation (ANR) method (Lane 1980)
- Assumes that the electron loses no energy in the inelastic collision
- Cross-section is expressed as a partial-wave expansion
- For low partial-waves contribution from FN T-matrices obtained via the R-matrix calculations: electronically elastic scattering
- Born approximation to obtain the cross section for the high partial-waves not included in the FN T-matrices (Crawford & Dalgarno 1971). Essential for dipolar molecules
- Final cross-section calculated as the sum of two contributions: can be regarded as a short-range correction to the Born approximation

\[
\frac{d\sigma_{j_0,\ell_0 \rightarrow j_f,\ell_f}}{d\Omega} = |f_{j_0,\ell_0 \rightarrow j_f,\ell_f}^B(\cos \theta)|^2 + \sum_{L=0}^{L_{\text{max}}} (A'_L - A''_L) P_L(\cos \theta)
\]
Disagreement between experiment and theory due to effect of dipole:
Experiment uses extrapolation procedure at forward angles
Theory needs top-up procedure to complete the partial wave expansion


Cho et al
Vibrational resolution in R-matrix calculations

Simple approach: use of Franck-Condon factors and equilibrium geometry ($R_0$) scattering data.

- Electronically inelastic scattering (and vibronically elastic)

Alternatively, vibrational averaging (adiabatic nuclei, AN)

- No energy balancing: works best when electronic energy curves are parallel (energy difference is the same for all geometries)

- Can’t model effect of resonances

- Used for diatomics but could in principle be used for normal modes of polyatomics

- Reduces to FN if T-matrix dependence on $R$ where vibrational wf is non-negligible is small (no good near thresholds)

$$F_{i\nu_i f \nu_f} = \left| \int \chi(R)_{i\nu_i} \chi(R)_{f \nu_f} dR \right|^2$$

$$\sigma(i \nu_i \rightarrow f \nu_f) = \sigma(i \rightarrow f) (R_0) F_{i\nu_i f \nu_f}$$

$$T_{l_i \nu_i, l_f \nu_f} = \int \chi_{\nu_f}(R)^{\text{FN}} T_{l_i \nu_i l_f}(R) \chi_{\nu_i}(R) dR$$
Vibrational resolution

- Transitions from ground vibronic state to lowest electronic excited state of BeH/BeD/BeT
- Size of vibrationally resolved cross sections very different for both models

Graphs showing cross sections for different initial energies and final vibrational states.
Other low energy approaches

Schwinger multichannel method (SMC)
- based on Lippmann–Schwinger integral equation
- applied within the FN approximation
- restricted to closed-shell molecular targets
- uses many strategies similar to R-matrix: GTOs used to bound and
  scattering orbitals, Hartree–Fock description for target state, Born top-up
  procedure…
- Elastic cross sections (integral and differential) of similar quality to R-matrix

SCMPP
- Analytic pseudopotentials used to describe the nuclei and core electrons
- Reduces computational cost
- Allows study of targets with electron-rich atoms (e.g. halogen atoms)

da Costa et al. EPJD 69 159 DOI: 10.1140/epjd/e2015-60192-6
Other low energy approaches

**Convergent close-coupling (MCCC)**
- For quasi-one and two-electron targets
- Uses close-coupling expansion
- Orbitals built from products of Laguerre polynomials, $\exp(-\alpha r)$ and spherical harmonic
- Works will at intermediate energies (pseudostates)
- Uses Born top-up
- Applied within the FN approximation but also beyond: AN for vibrationally resolved calculations
- Vibrational wavefunctions are obtained diagonalizing the vibrational Hamiltonian in a basis of above Laguerre functions
- Integral and differential cross-sections for elastic, vibration and electronic excitation, ionization and neutral dissociation

Zammit et al 2017  JPB 50 123001
DOI 10.1088/1361-6455/aa6e74
Scarlett et al 2020 EPJD 74 36
DOI 10.1140/epjd/e2020-100549-0
$H_2$

- Simplest multielectronic molecule
- High quality calculations available and converged

Excellent agreement between theoretical methods: UKRmol+ (R-matrix) and MCCC (molecular convergent close-coupling)

Meltzer et al, JPB 53 (2020) 145204
What is still hard at low energies

- Calculations for
  - very big or electron rich targets
  - vibrationally resolved cross sections for molecules with many vibrational modes
- Very accurate elastic cross sections for dipolar molecules
- Data for molecules not initially in their ground state
- Neutral dissociation and dissociative electron attachment (DEA) beyond triatomics (and even then….). Experiment can measure DEA (in general yields not cross sections) but neutral dissociation is very hard
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