Low temperature chemistry using the R-matrix method

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H⁺ + H → H₂
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Cold and ultracold molecules

Low-energy collision processes

Elastic scattering
\[ \text{HD}(v,J) + H^+ \rightarrow \text{HD}(v,J) + H^+ \]

Inelastic scattering
\[ \text{HD}(v,J) + H^+ \rightarrow \text{HD}(v',J') + H^+ \]

Reactive scattering
\[ \text{HD} + H^+ \rightarrow \text{H}_2 + D^+ \]

Charge exchange
\[ \text{HD} + H^+ \rightarrow \text{HD}^+ + H \]

Photodissociation
\[ \text{H}_2\text{D}^+ + hv \rightarrow \text{HD}(v,J) + H^+ \]

Radiative association
\[ \text{HD} + H^+ \rightarrow \text{H}_2\text{D}^+ + hv \]

Predissociation
not important for \( \text{H}_2\text{D}^+ \)

Long-range, weakly-bound states
$H_2$ vibrational wavefunctions
H$_3^+$ vibrational wavefunctions near dissociation

Near threshold photodissociation spectrum of H$_3^+$

Low energy collisions with systems with deep potential wells

Naturally divide into two regions:
Long-range:
• simple s-wave scattering
Short-range:
• complicated structures even near threshold
• many resonances
The R-matrix method

PG Burke, R-Matrix Theory of Atomic Collisions Application to Atomic, Molecular and Optical Processes (Springer, 2011)

R-Matrix theory:

1940s Introduced by Wigner & Eisenbud for nuclear physics: phenomenological

1960s Calculable theory for electron – atom/ion collisions (Burke et al)

1970s Calculable electron-molecule collisions (Schneider, Burke and others) (Phenomenological also used by Fabrikant, Meyer, etc)

1980s Light-Walker propagator for reactive scattering

Present: Calculable R-matrix is method of choice for electron collision calculations also time-dependent (fast laser studies) used in nuclear physics and elsewhere
UK Atomic Molecular R-matrix code base

- **e-atom/ion**
  - PRMAT
  - p-Rmatrix I
  - pDARC
  - RINIT
  - RMT
  - Time-dependent

- **e-molecule**
  - UKRMol
  - UKRMol+
  - Swinterf
  - PFARM
  - pstgf
  - pstgbf
  - Time-independent

- **heavy-particle**
  - DVR3D
  - WAVR4
  - TROVE
  - RMatReact
  - Inner region
  - Boundary region
  - Outer region
RmatReact treatment of reactive scattering

What is an $R$-matrix?
Relates (asymptotic) radial wavefunction to its derivative

\[
R(r, E) = \frac{F(r)}{F'(r)}
\]

where $F_i(r)$ is the asymptotic radial wavefunction associated with channel $i$.

Each channel is associated with an asymptotic state \( Eg \) in \( H^+ + H_2 \),
\( i \) represents \( (\nu, J) \) states of \( H_2 \).
On the R-matrix boundary, \( r=a \)

\[
R_{i,j}(E) = \frac{1}{2a} \sum_k \frac{\omega_{k,i} \omega_{k,j}}{E - E_k}
\]

where \( E_k \) is the energy of the \( k^{\text{th}} \) inner region solution and \( w_{i,k} \) is the amplitude of this solution in channel \( i \)

In the inner region

- Continuum wavefunctions are discretised
- Solutions do not depend on scattering energy
RmatReact summary

Flexible RmatReact harness for inner region codes

Frame transformation (on the boundary):
- Hyperfine coupling
- Spin-orbit coupling
- Magnetic fields
L.K. McKemmish and J. Tennyson,
General Mathematical Formulation of Reactive Atom-Diatomic Collisions in RmatReact Methodology
Inner region: variational nuclear motion programs

- Duo: vibronic spectra of diatomics implementation complete
- DVR3D: triatomics (exact kinetic energy) partial implementation
- WAVR4: tetratomics (exact kinetic energy) to be done
- TROVE: polyatomic (approx. kinetic energy) to be done
New general diatomic code

Duo

Duo: A general program for calculating spectra of diatomic molecules

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Hund’s case (a)

\[ \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + \hat{R}^2 \]

Total angular momentum

\[ \hat{L} \]

Electronic angular momentum

\[ \hat{S} \]

Spin

\[ \hat{R} \]

Rotational angular momentum

\[ \phi_n = |v\rangle|J\Omega\rangle|S\Sigma\rangle|L\Sigma\rangle \]

Vibrational

Spin

Rotational

Electronic
J Tennyson, L Lodi, LK McKemmish & SN Yurchenko,
The ab initio calculation of spectra of open shell diatomic molecules,
CaO: potential energy curves
CaO: transition dipole moment curves
CaO
Curve-couplings

Spin-orbit

bond length, Å

Spin-orbit, cm$^{-1}$

EAMC: $L_y$

$\langle \Psi' | \hat{L}_x | \Psi'' \rangle$

$E_{\text{AMC}} : L_y$

$E_{\text{AMC}} : L_{y1}$

$E_{\text{AMC}} : L_{y1A}$

$E_{\text{AMC}} : L_{y3}$
CaO: line list

Duo implementation:

- Bloch term to allow for finite boundary
- Lobatto Shape function DVR used
- Initial tests on Ar – Ar (elastic scattering)
- Study of He – O(3Pj) (inelastic scattering)
- Code available on gitlab (via www.exomol.com)
Eigenphases for the Morse potential

T. Rivlin, L.K. McKemmish and J. Tennyson,
Low temperature scattering with the R-matrix method: the Morse potential,
Springer Conference Proceedings. (in press)
Ar – Ar inner region wavefunctions with Duo

Ar – Ar low energy eigenphases: J=5
Ar – Ar total cross section at low energy

Structure of the S-matrix in the complex k-plane

$E = \frac{k^2}{2}$

PS Bingham & JD Gorfinkiel,
Reskit: A toolkit to determine the poles of an S-matrix
Ar – Ar bound state as pole in S-matrix in the complex k-plane.
RmatReact: current status

- Ar – Ar elastic collisions: completed
- \( \text{O}(^3\text{P}_j) \) – He inelastic collisions: nearing completion
- Triatomics (DVR3D) development in progress
- Collaboration with Brianna Heazlewood (Oxford) on ultralow energy ion – molecule collisions
About the first edition
“The best book for anyone who is embarking on research in astronomical spectroscopy”
Contemporary Physics (2006)

3rd edition published 18 June 2019