Low temperature chemistry using the R-matrix method

H^+

H — H

Jonathan Tennyson

University College London

Outer region

Inner region

Few Body Systems
Surrey
Sept 2019

The RmatReact Team

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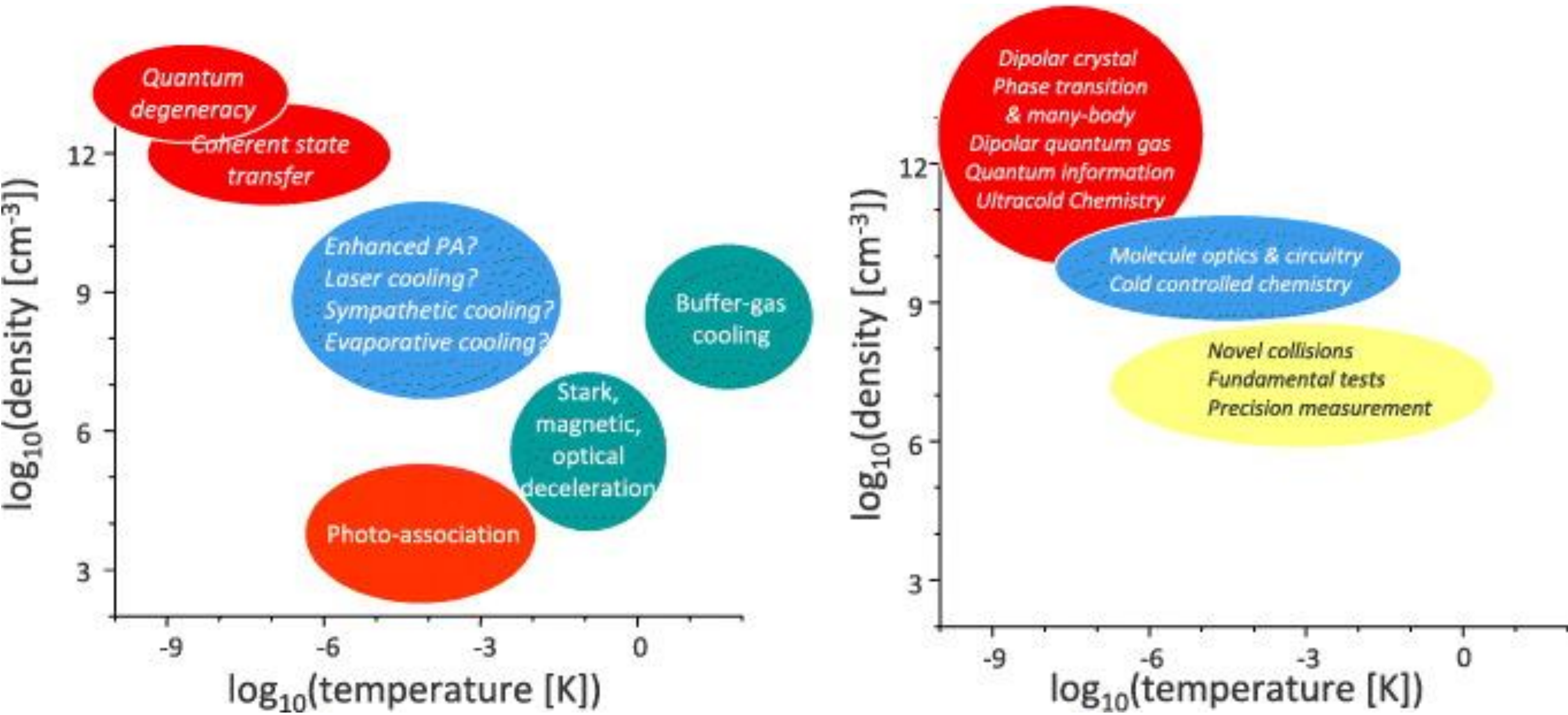
Contents

Cold and ultracold molecules



LD Carr, D DeMille, RV Krems, J Ye, New. J. Phys., 11, 055049 (2009)

Low-energy collision processes

H_2D^+ as an example

Elastic scattering

$HD(v,J) + H^+ \longrightarrow HD(v,J) + H^+$

Inelastic scattering

$HD(v,J) + H^+ \longrightarrow HD(v',J') + H^+$

Reactive scattering

$HD + H^+ \longrightarrow H_2 + D^+$

Charge exchange

$HD + H^+ \longrightarrow HD^+ + H$

Photodissociation

$H_2D^+ + h\nu \longrightarrow HD(v,J) + H^+$

Radiative association

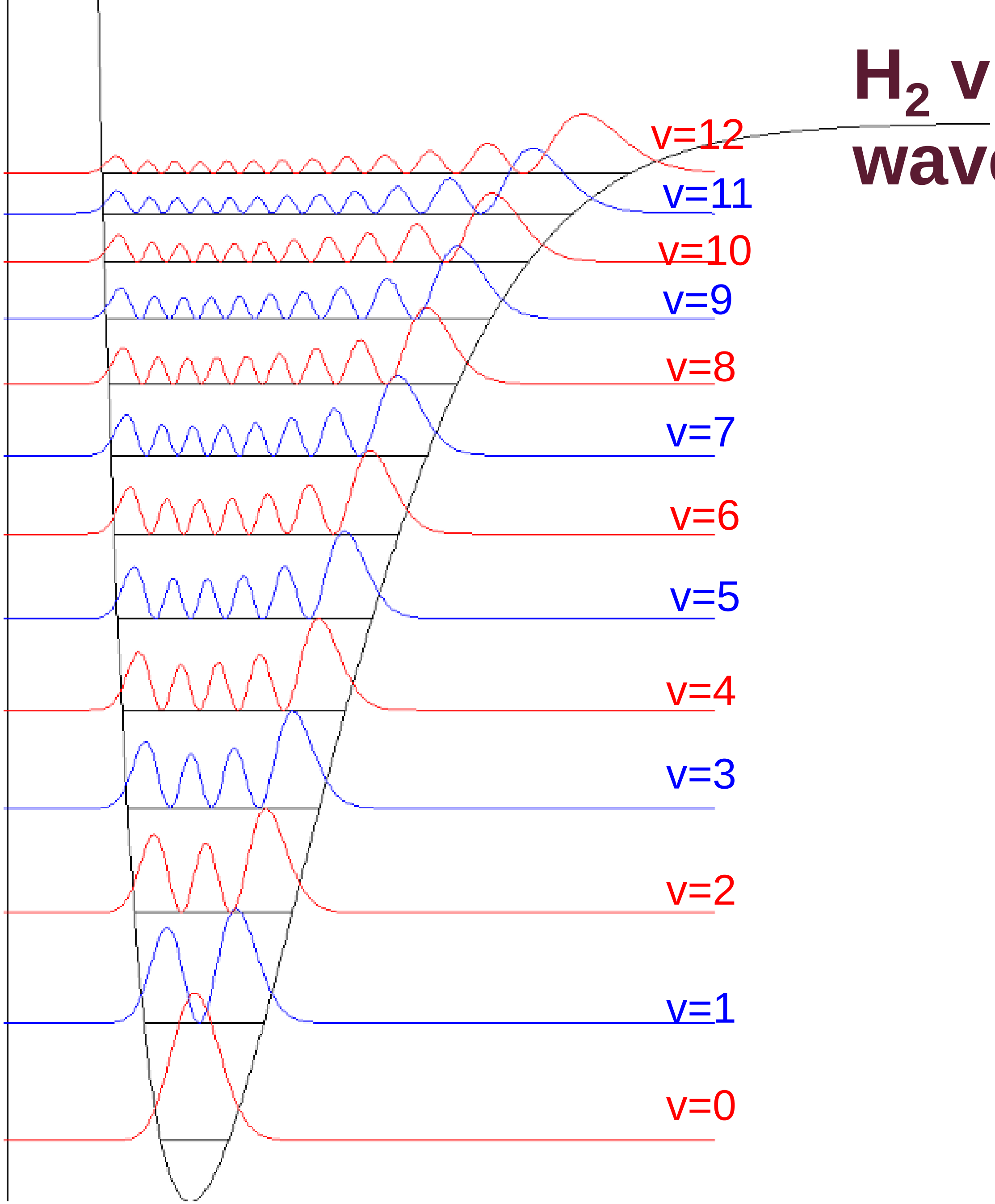
$HD + H^+ \longrightarrow H_2D^+ + h\nu$

Predissociation

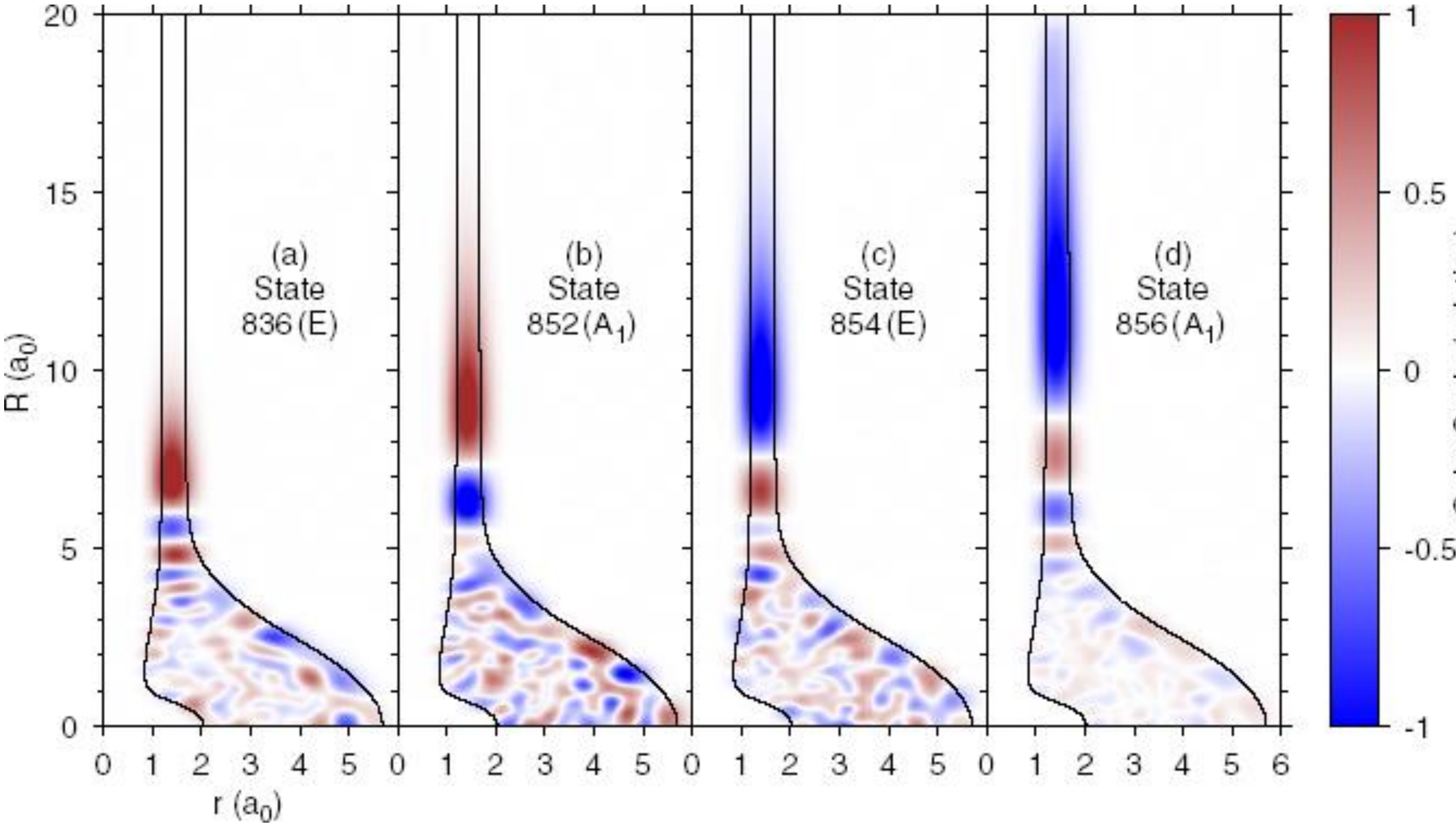
not important for H_2D^+

Long-range, weakly-bound states

H_2 vibrational wavefunctions

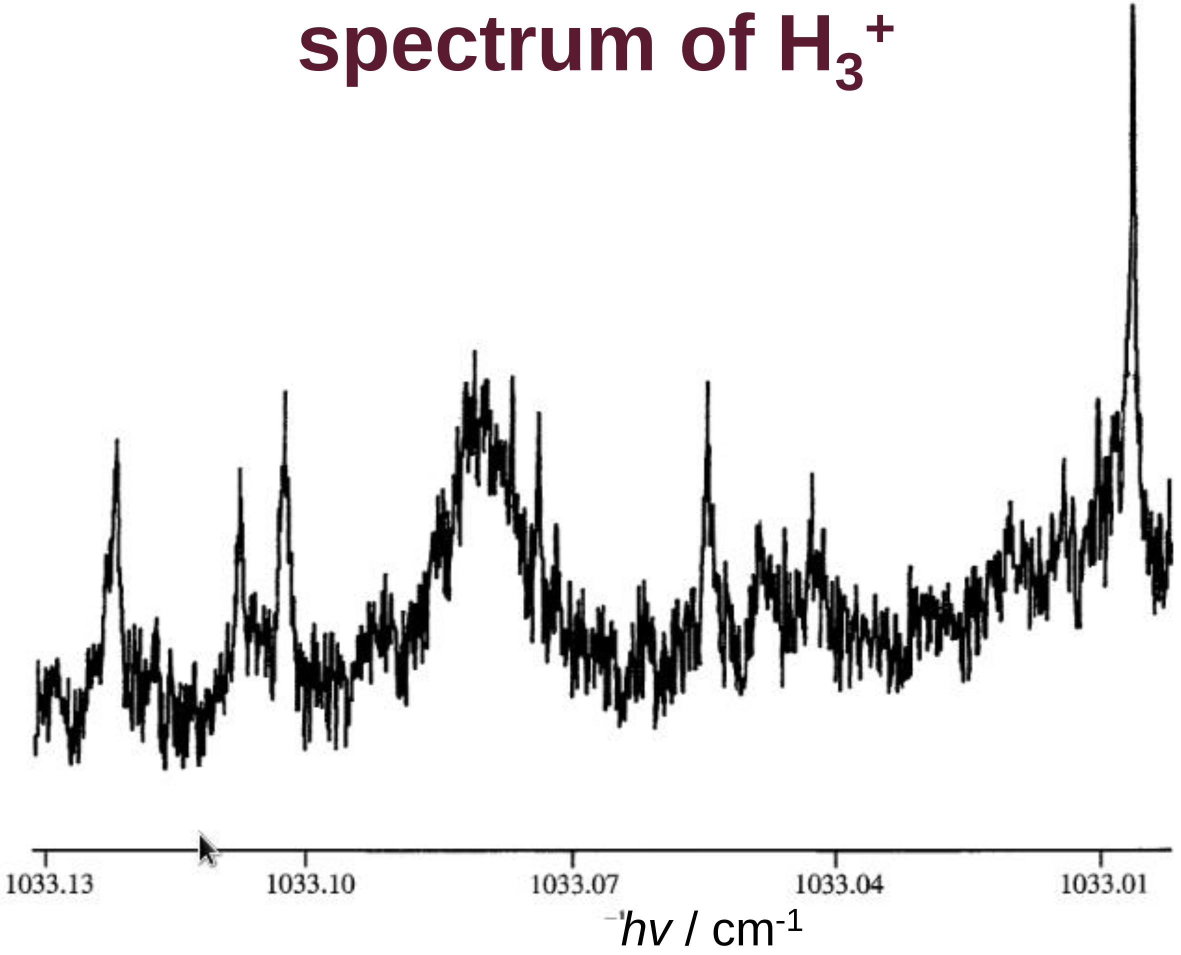


H_3^+ vibrational wavefunctions near dissociation



J.J. Munro, J. Ramanlal & J. Tennyson, New J. Phys., 7, 196 (2005)

Near threshold photodissociation spectrum of H_3^+



F Kemp, CE Kirk & IR McNab Phil. Trans. R. Soc. Lond. A 358, 2403 (2000).

Low energy collisions with systems with deep potential wells

Naturally divide into two regions:

Long-range:

- simple s-wave scattering

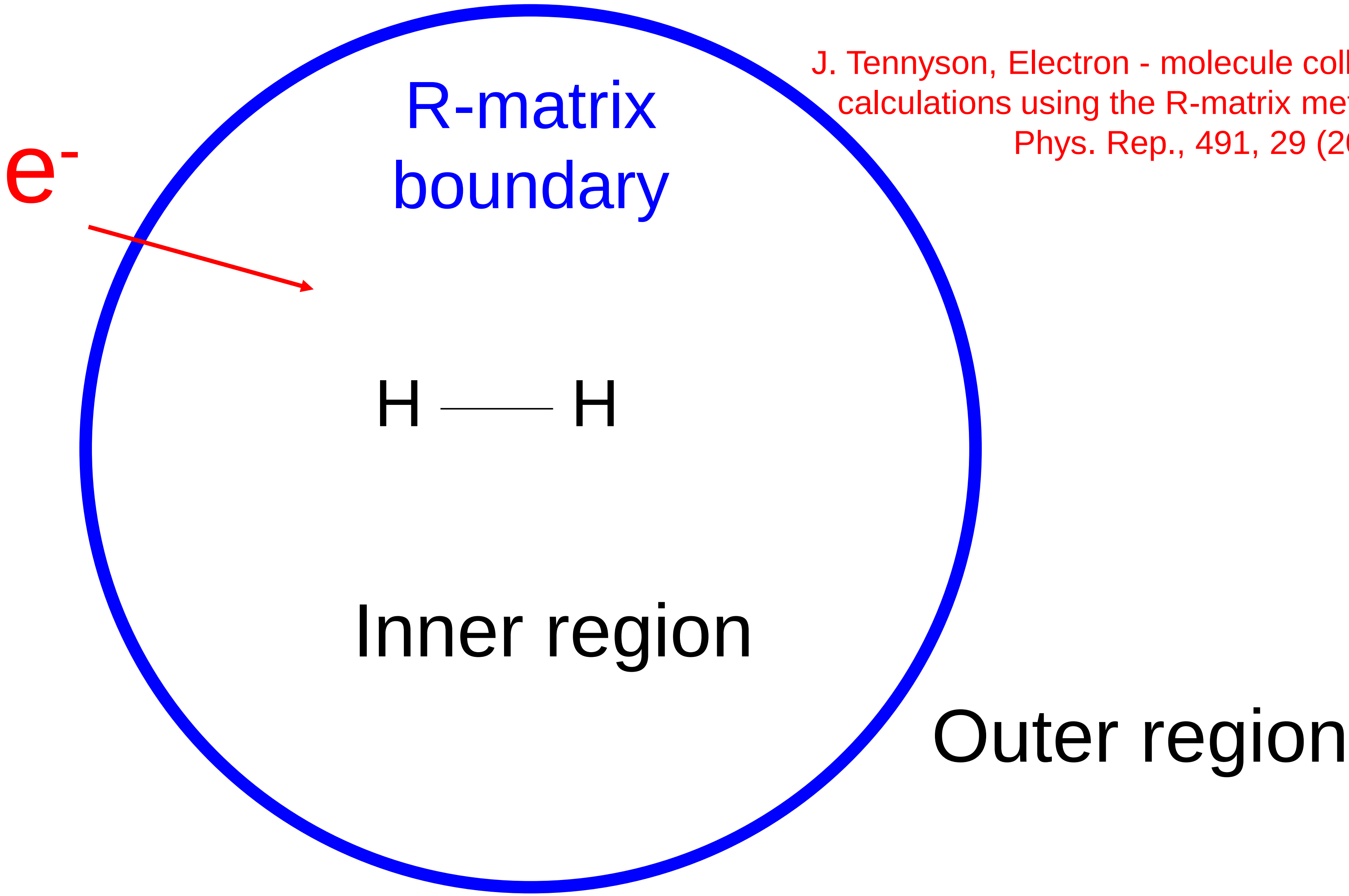
Short-range:

- 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)

J. Tennyson, Electron - molecule collision calculations using the R-matrix method, Phys. Rep., 491, 29 (2010).



R-Matrix theory:

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

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

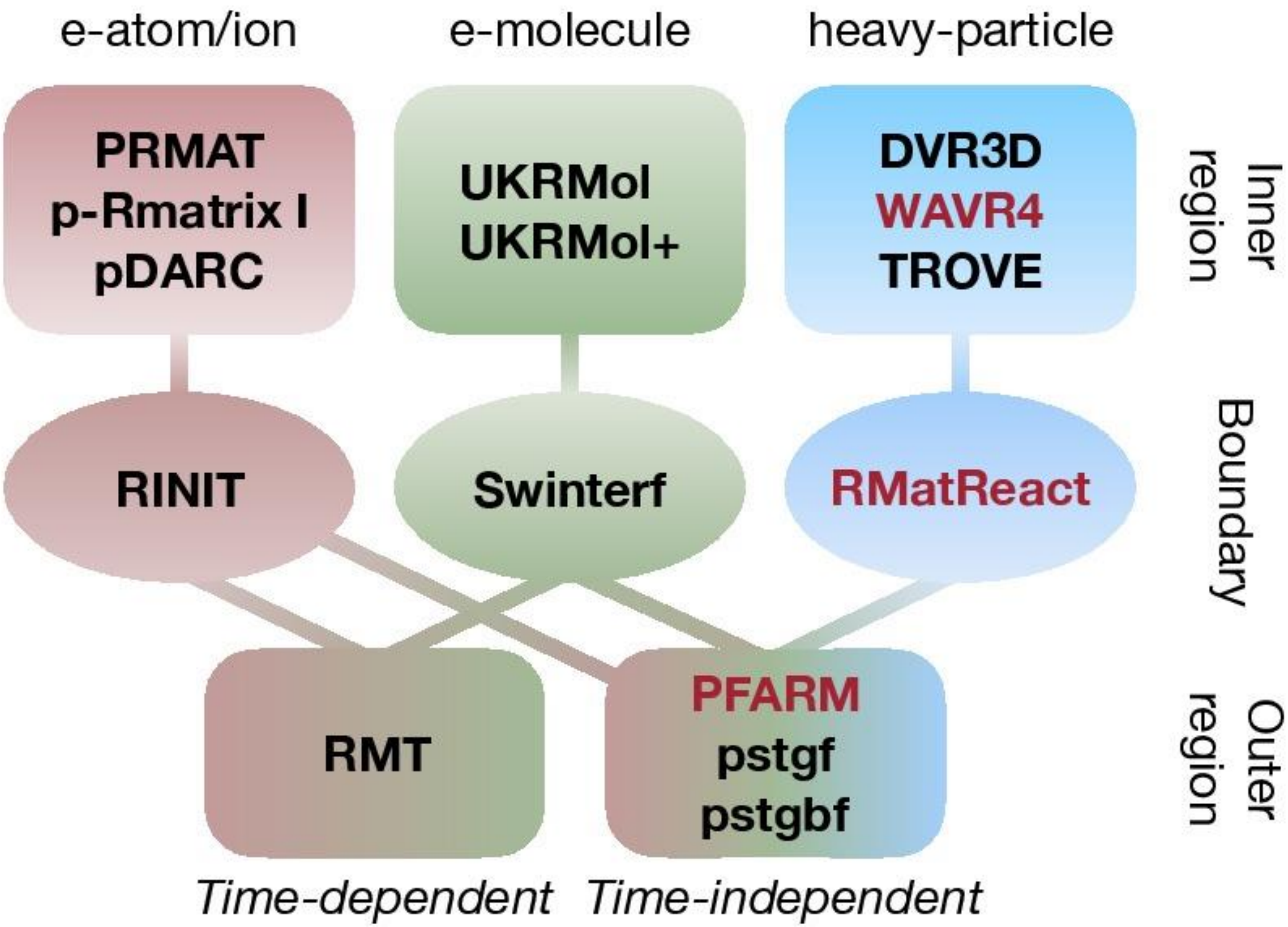
1970s Calculable electron-molecule collisions (Schneider, Burke and others)
(Phenomenological also used by Fabrikant, Meyer, etc)

1980s Light-Walker propagator for reactive scattering

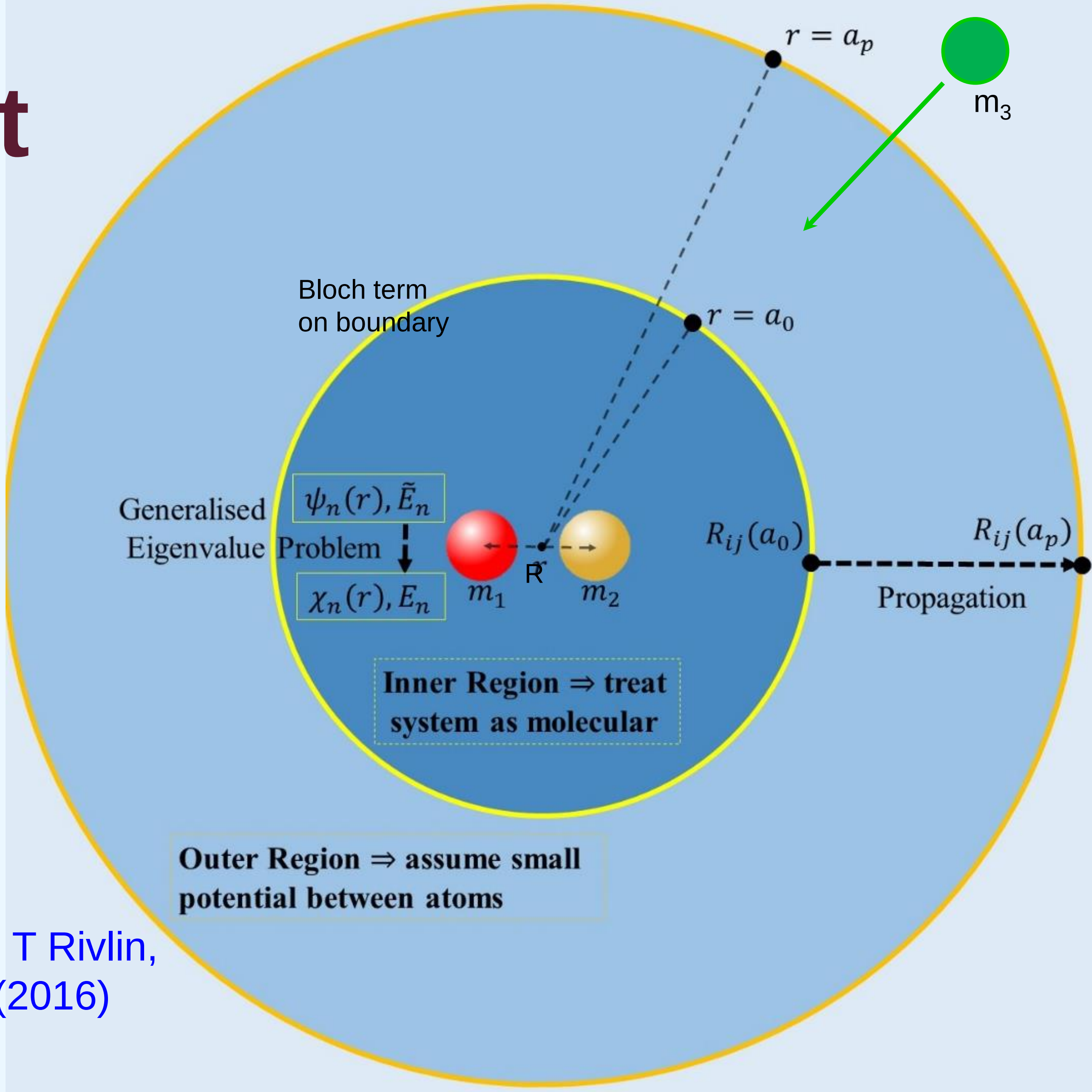
Present: Calculable R-matrix is method of choice for electron collision calculations
also time-dependent (fast laser studies)
used in nuclear physics and elsewhere

CCPQ

UK Atomic Molecular R-matrix code base



RmatReact
treactment of reactive scattering



J Tennyson, LK McKemmish, T Rivlin,
Faraday Discussion **195**, 31 (2016)

What is an R-matrix?

Relates (asymptotic) radial wavefunction to its derivative

$$\mathbf{R}(r,E) = \frac{\mathbf{F}(r)}{\mathbf{F}'(r)}$$

$$R_{i,j}(r,E) = \frac{F_i(r)}{F_j'(r)}$$

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 *(v,J)* states of H_2.

On the R-matrix boundary, *r=a*

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

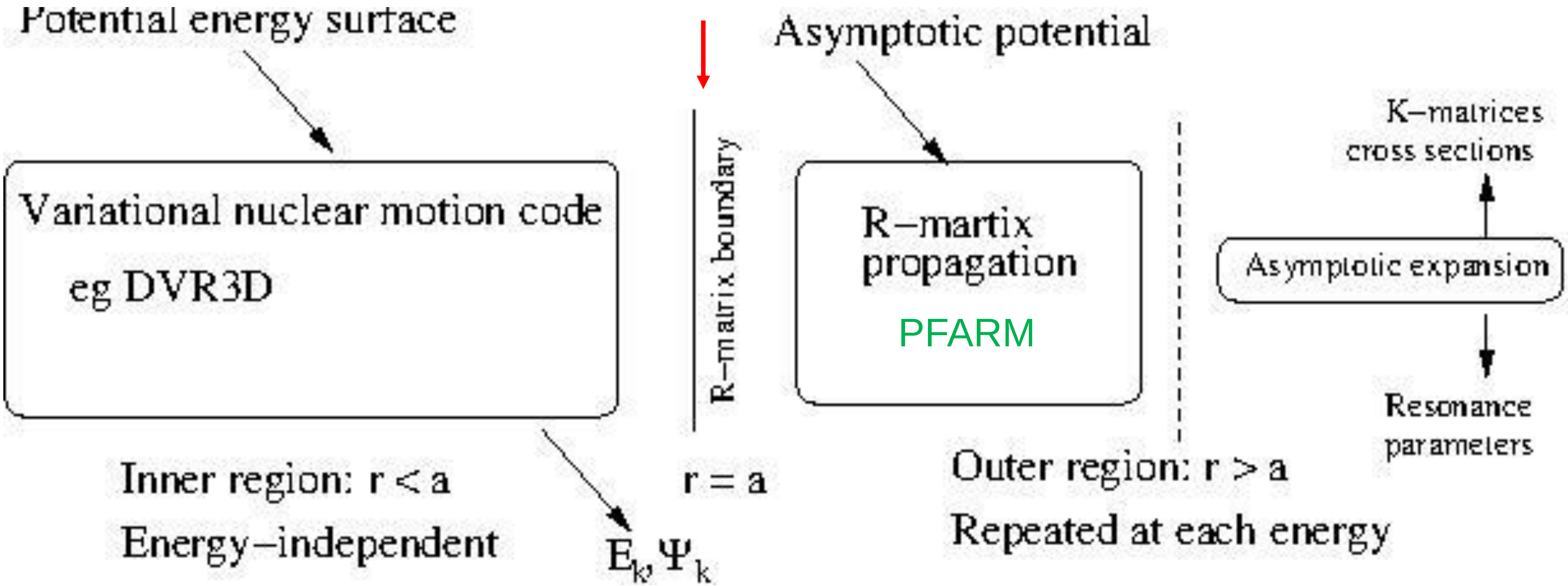
where E_k is the energy of the k^{th} inner region solution and $w_{i,k}$ is the amplitude of this solution in channel i

In the inner region

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

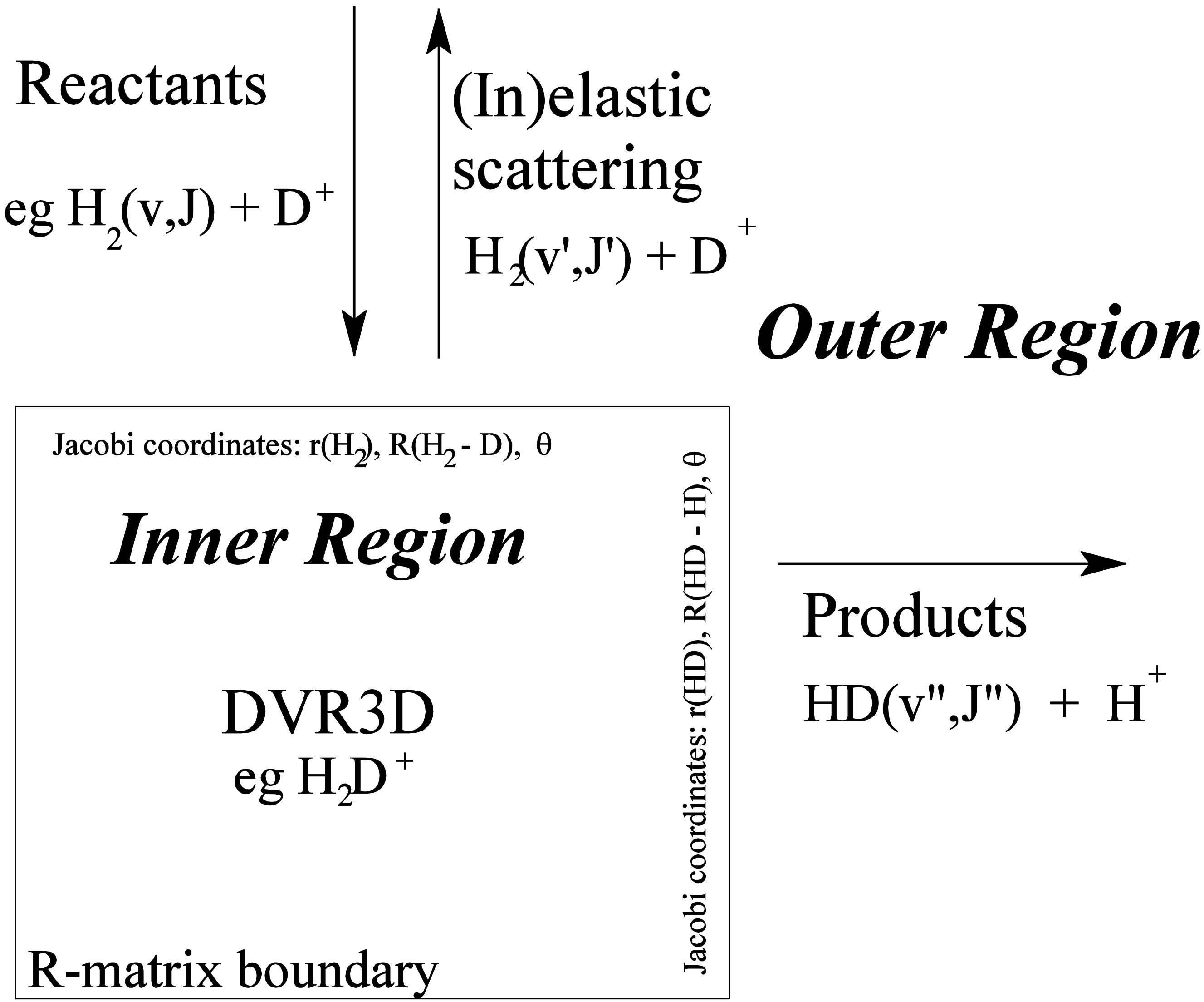
RmatReact summary

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
Phil. Trans. Royal Soc. London A, **377**, 20180409 (2019).

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

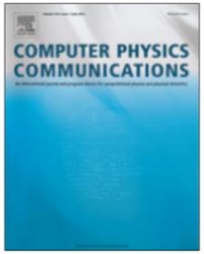
New general diatomic code
Duo

Computer Physics Communications 202 (2016) 262–275

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc

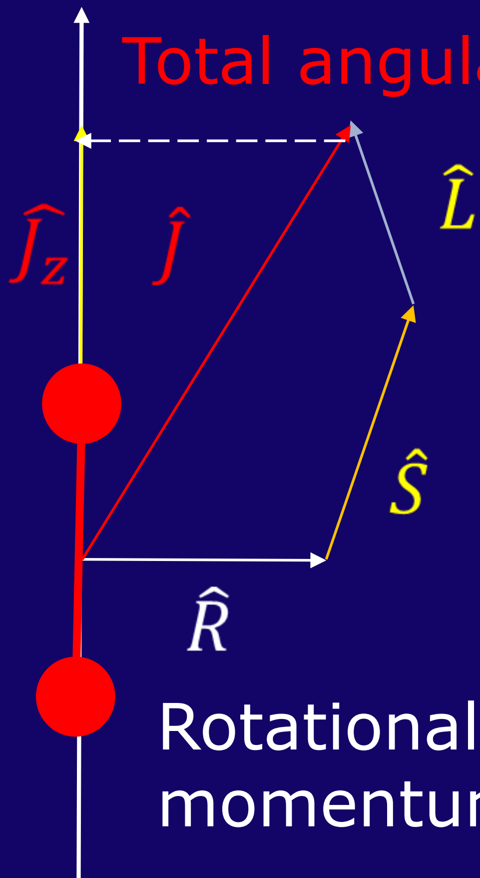


Duo: A general program for calculating spectra of diatomic molecules☆

Sergei N. Yurchenko [a,*], Lorenzo Lodi [a], Jonathan Tennyson [a], Andrey V. Stolyarov [b]

[a] *Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*

Hund's case (a)



Total angular momentum

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

Electronic angular momentum

Spin

Vibrational Spin

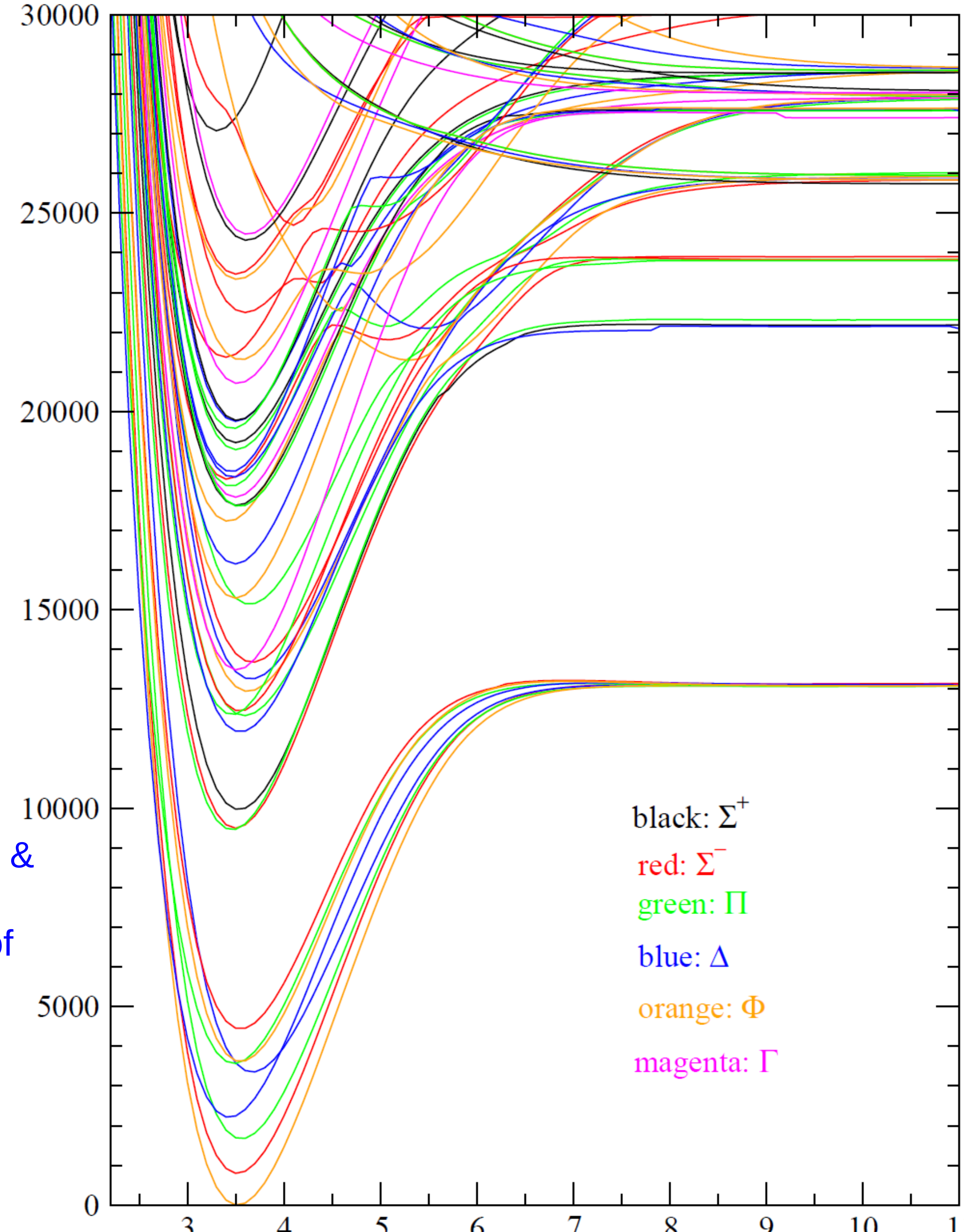
$$\phi_n = |v\rangle|J\Omega\rangle|S\Sigma\rangle|LS\Sigma\rangle$$

Rotational Electronic

Rotational angular momentum

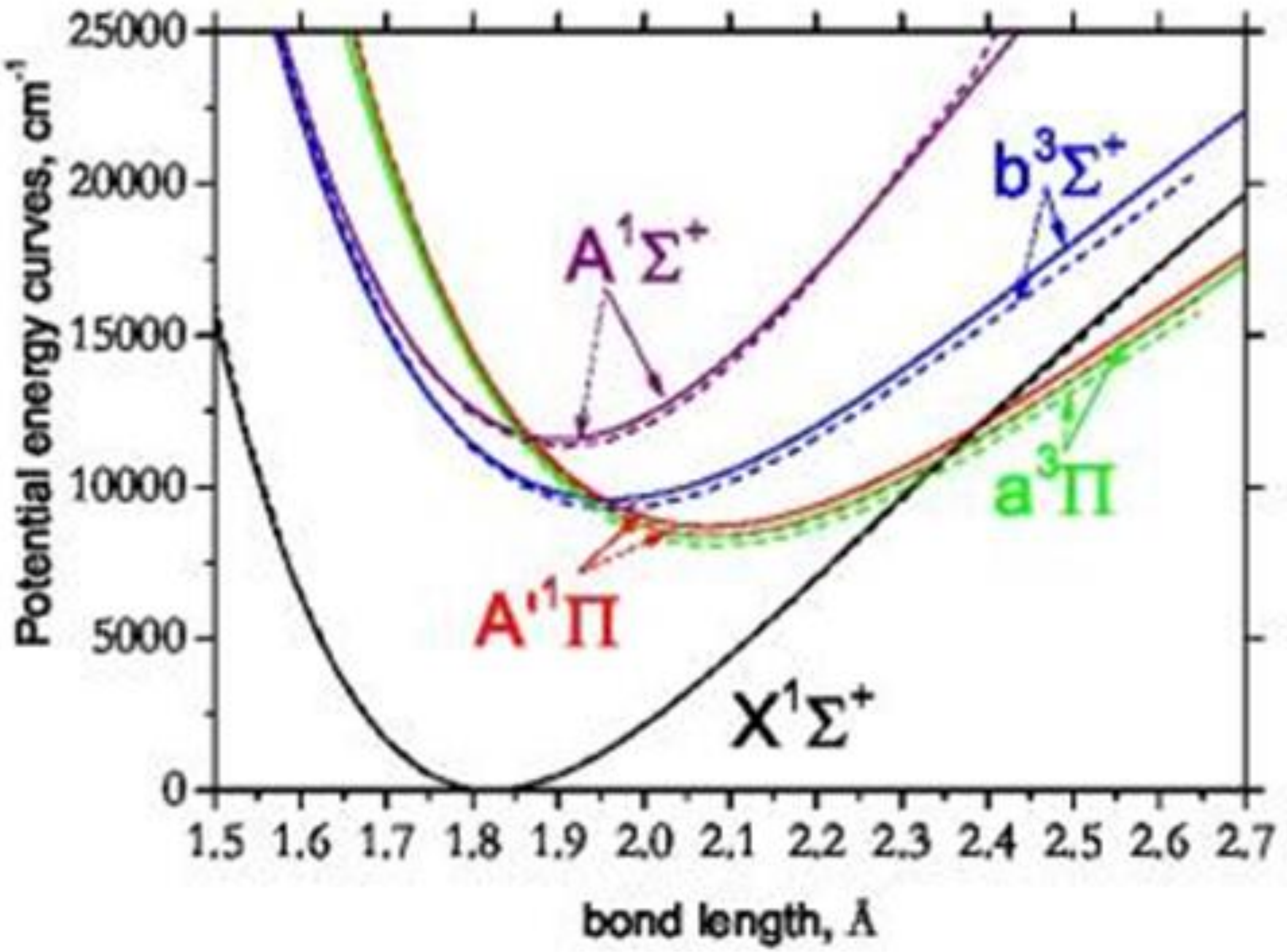
TiH

Lorenzo Lodi

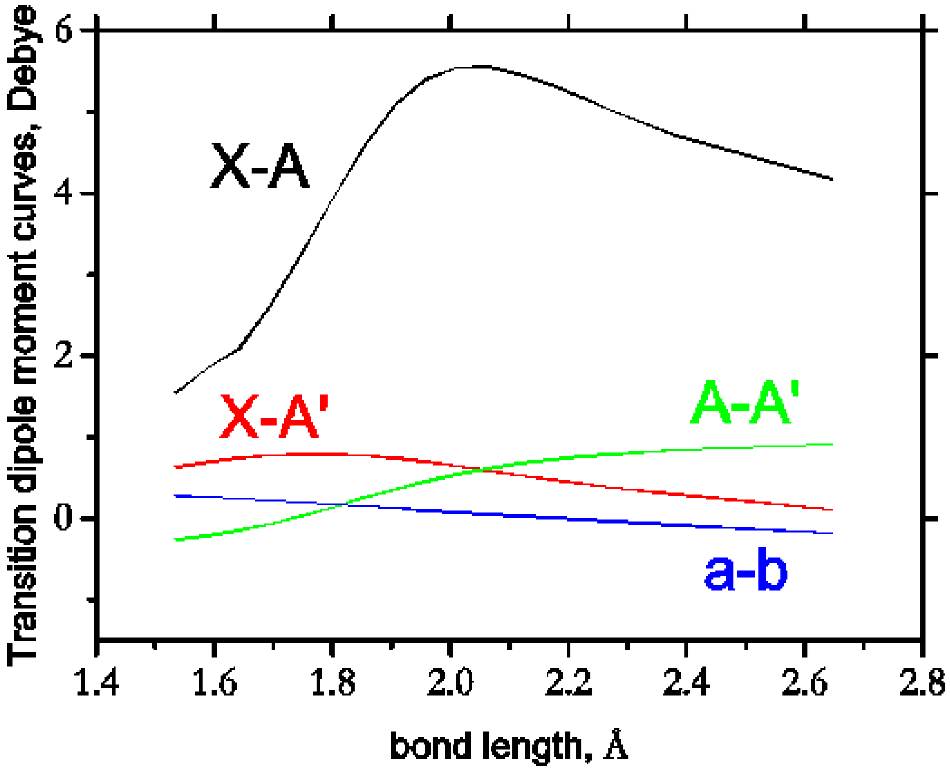


J Tennyson, L Lodi, LK McKemmish & SN Yurchenko,
The ab initio calculation of spectra of open shell diatomic molecules,
J. Phys. B, 49, 102001 (2016)
(Topical Review)

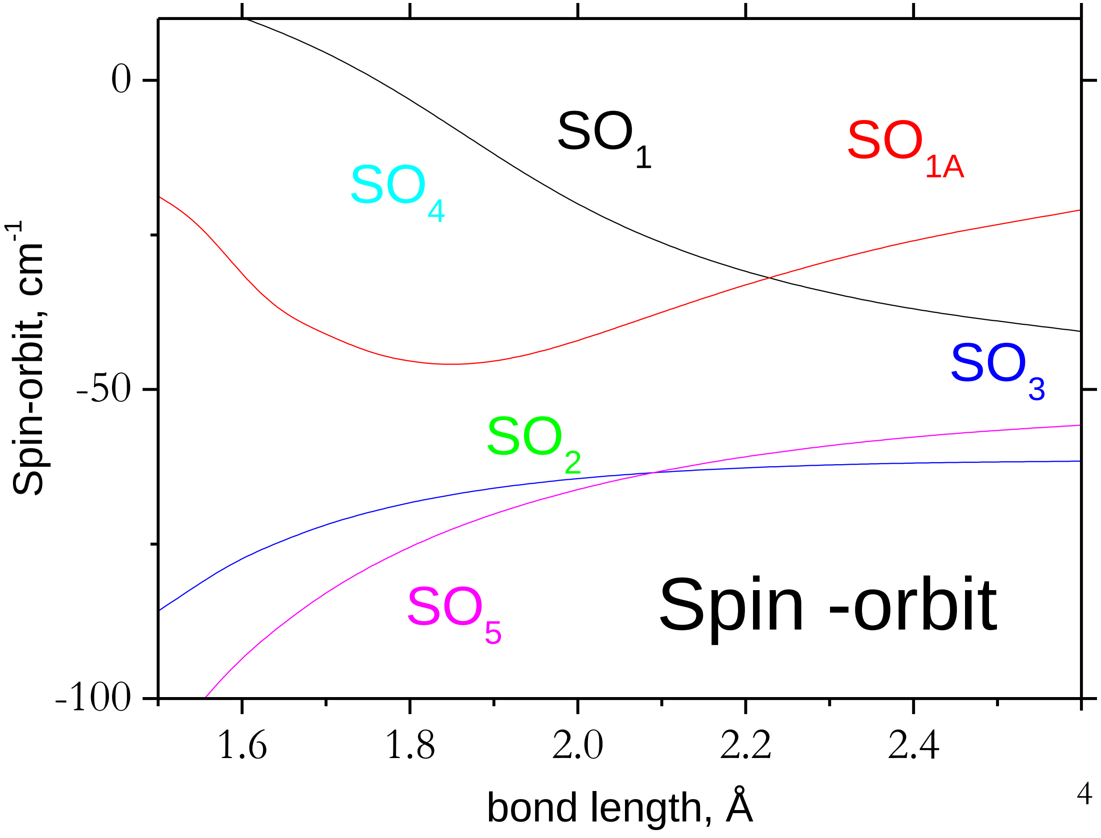
CaO: potential energy curves

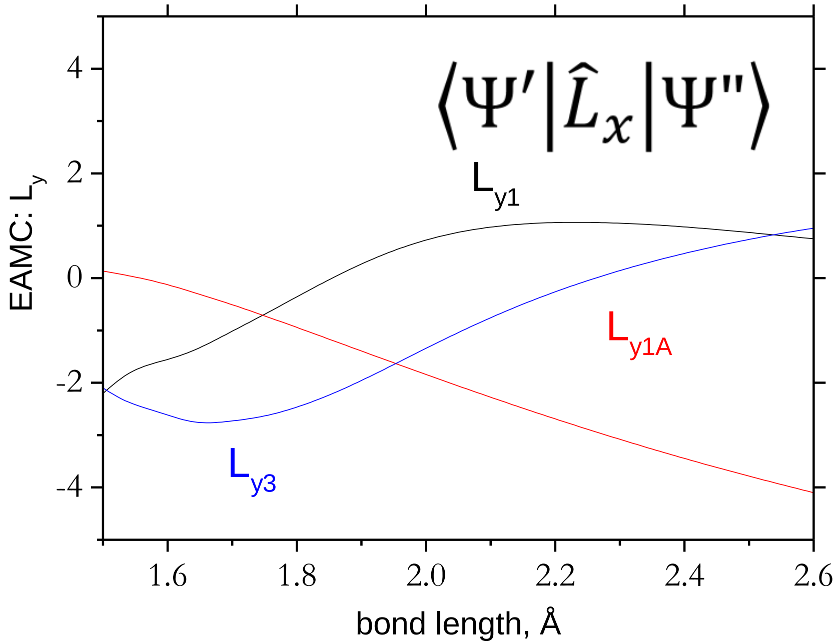


CaO: transition dipole moment curves

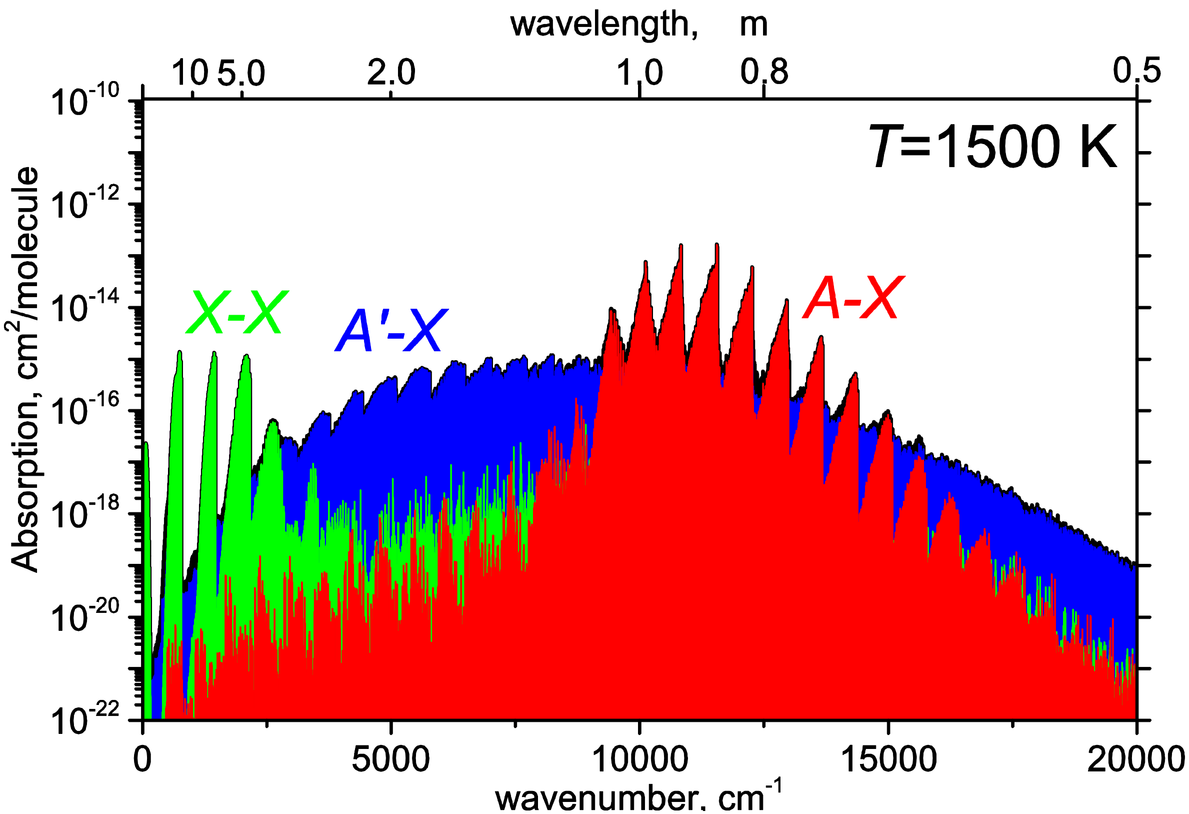


CaO
Curve-couplings





CaO: line list



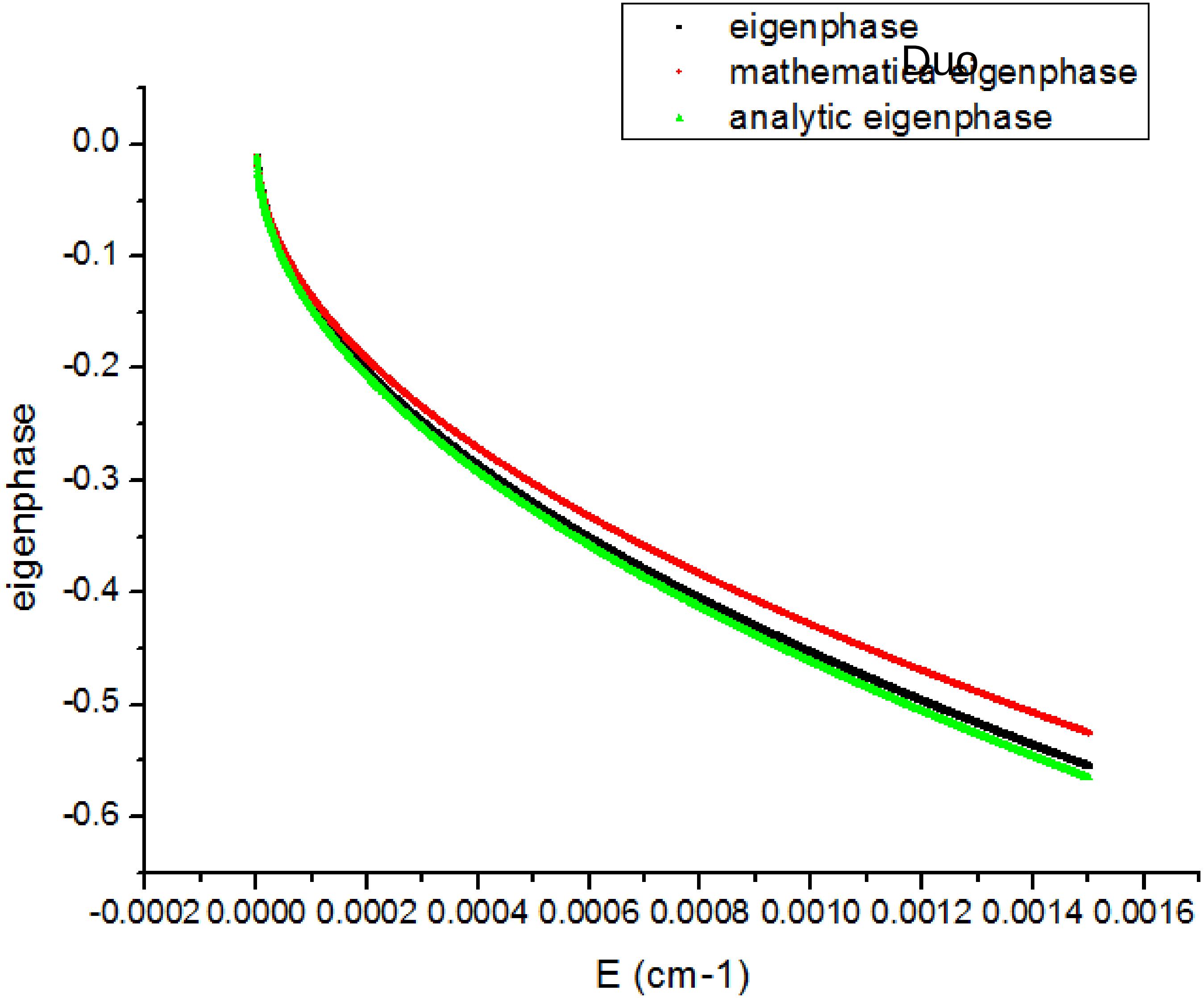
Line list: 22 M lines

S.N. Yurchenko, A. Blissett, U. Asari, M. Vasilios, C. Hill & J. Tennyson, Mon. Not. R. astr. Soc., 456, 4524 (2016)

Duo implementation:

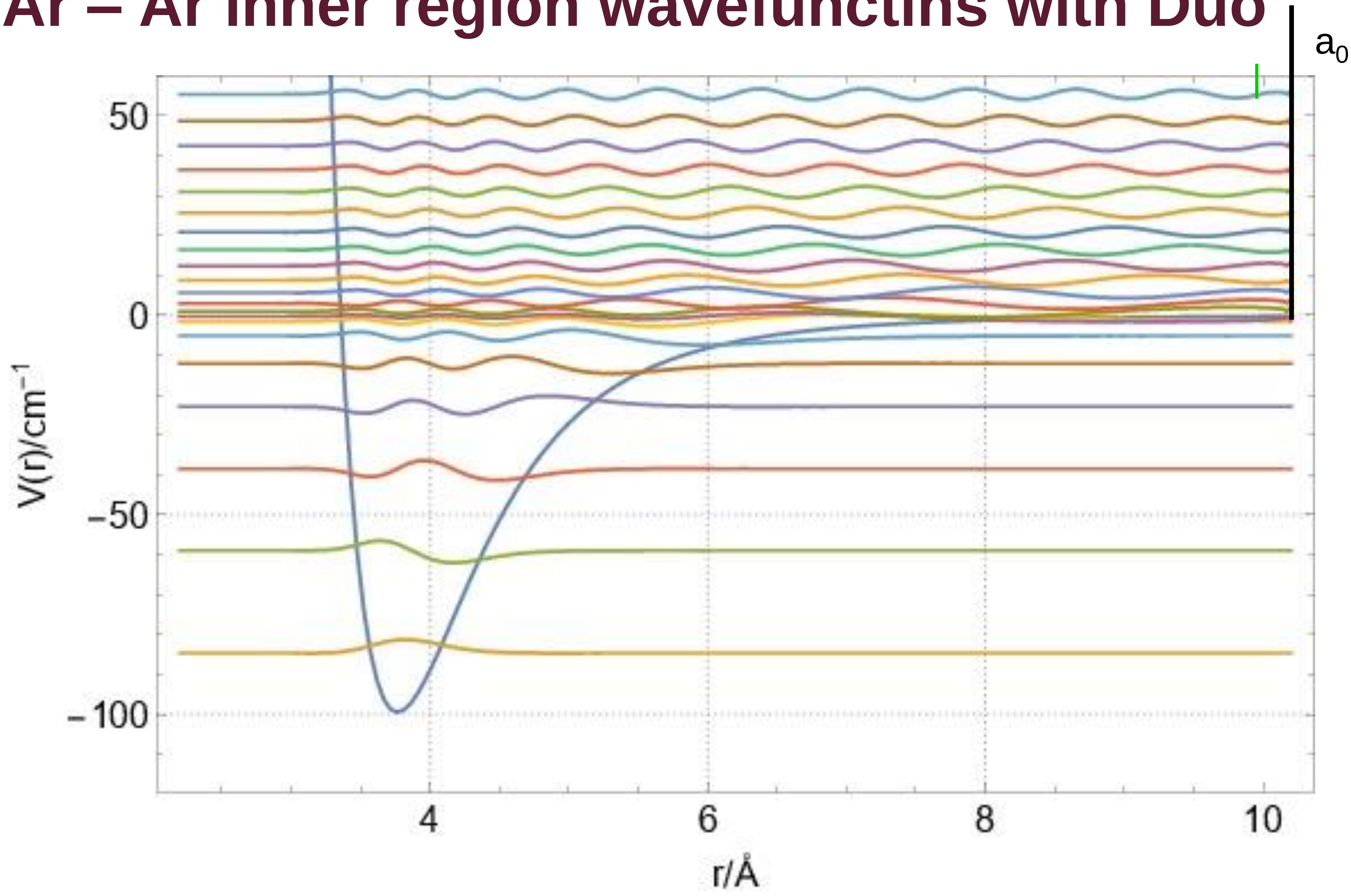
- Bloch term to allow for finite boundary
- Lobatto Shape function DVR used
- Initial tests on Ar – Ar (elastic scattering)
- Study of He – O(^3P_j) (inelastic scattering)
- Code available on gitlab (via www.exomol.com)

Eigenphases for the Morse potential



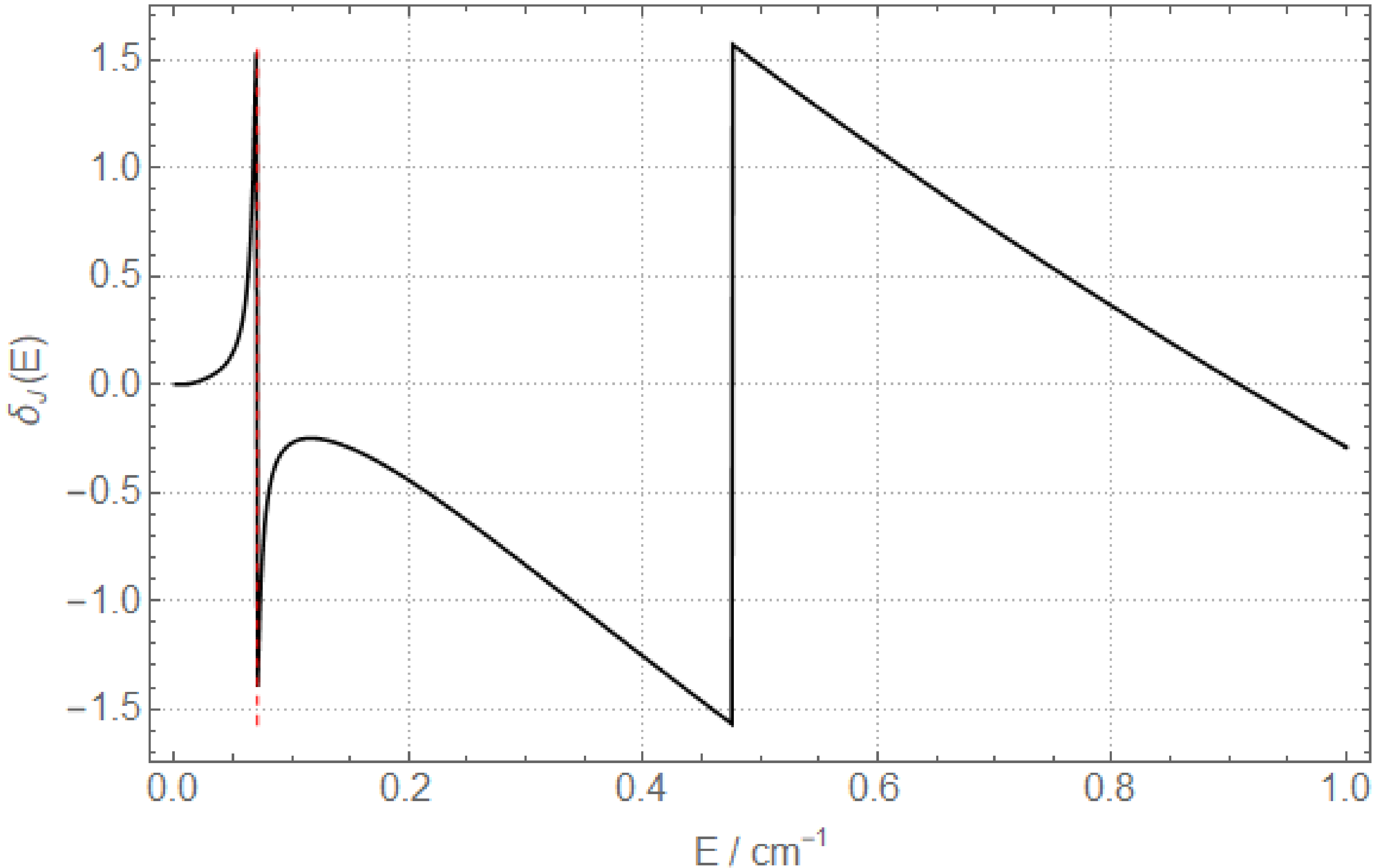
T. Rivlin, L.K. McKemmish and J. Tennyson,
Low temperature scattering with the R-matrix method: the Morse potential,
Springer Conference Proceedings. (in press)

Ar – Ar inner region wavefunctins with Duo

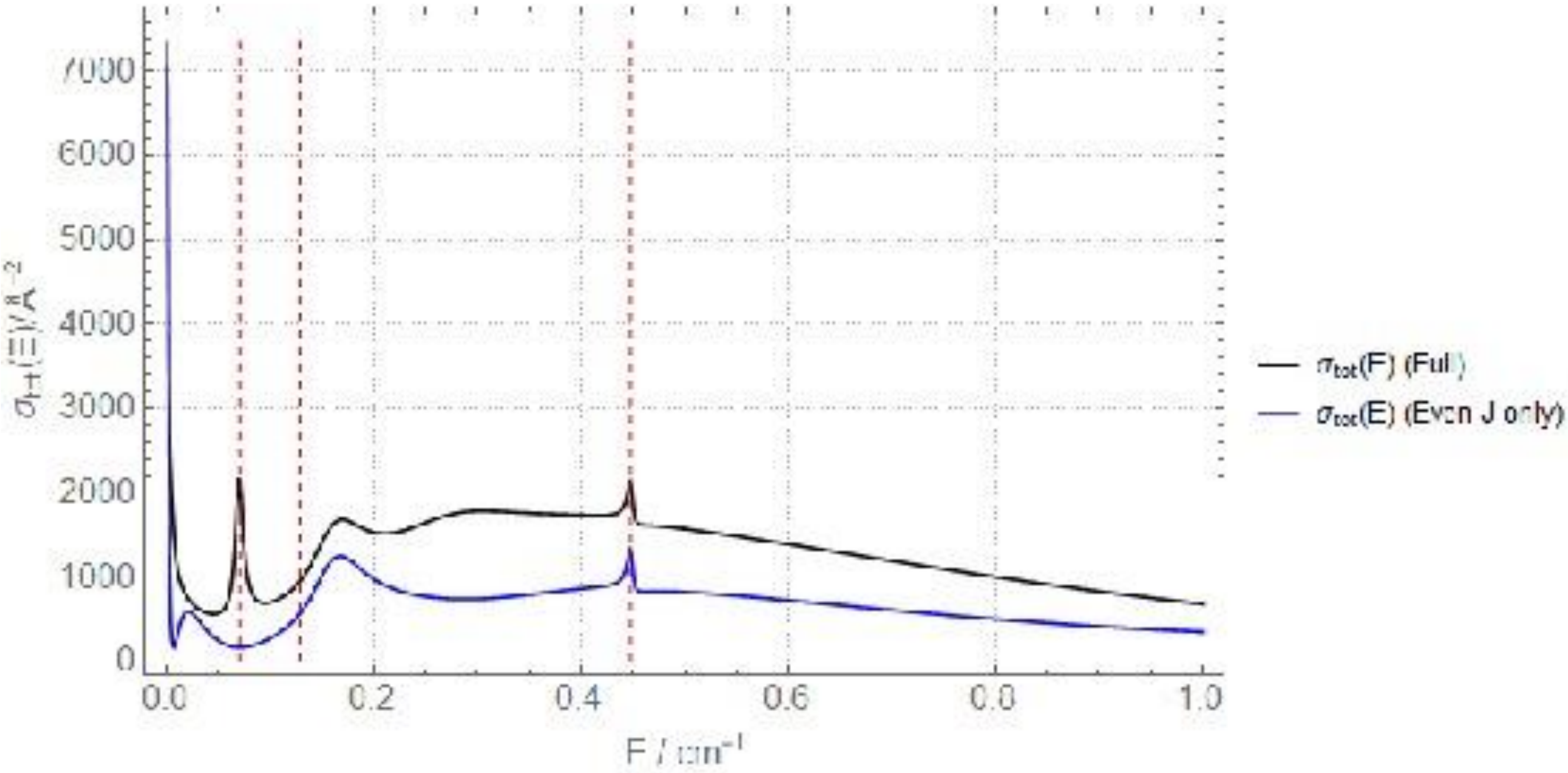


T. Rivlin, LK McKemmish, KE Spinlove & J Tennyson, Mol. Phys. (in press)

Ar – Ar low energy eigenphases: J=5



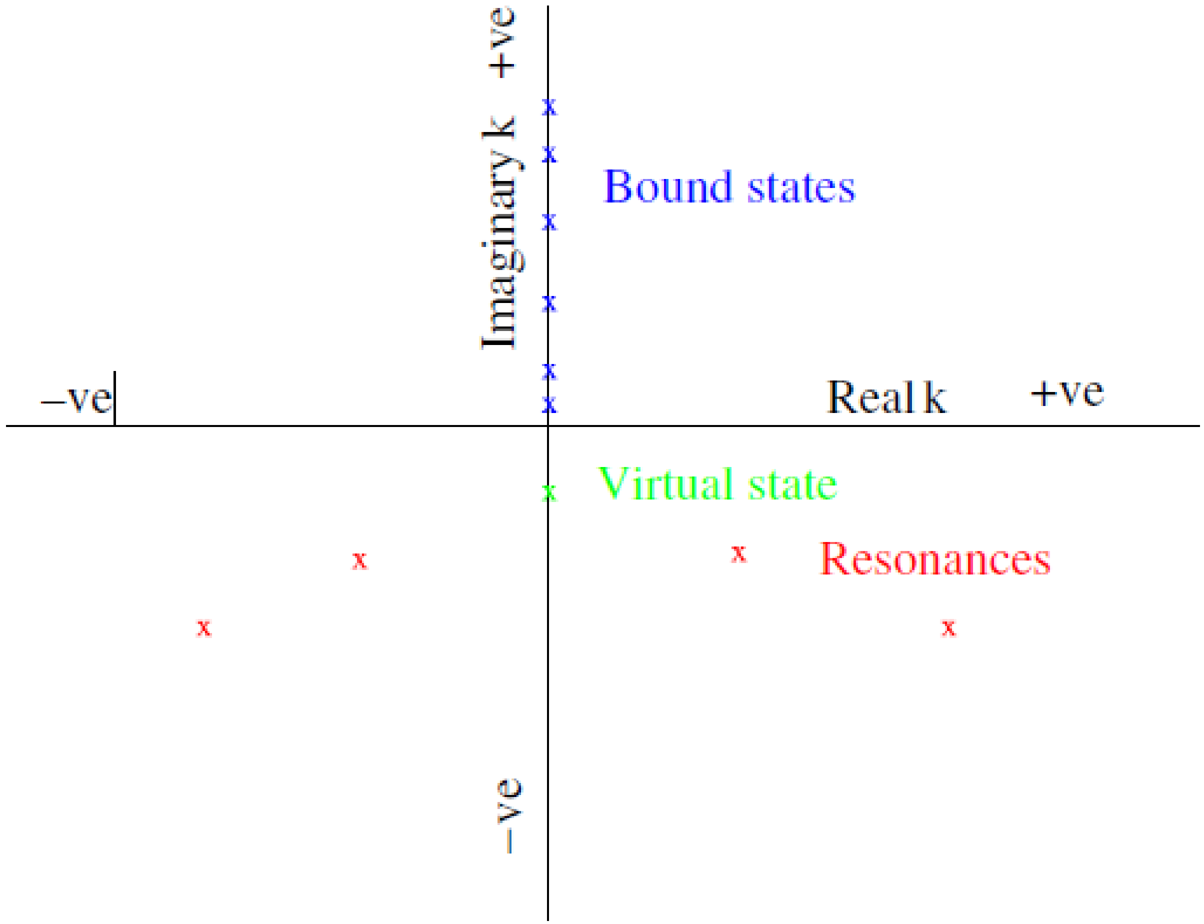
Ar – Ar total cross section at low energy



T. Rivlin, LK McKemmish, KE Spinlove & J Tennyson, Mol. Phys. (in press)

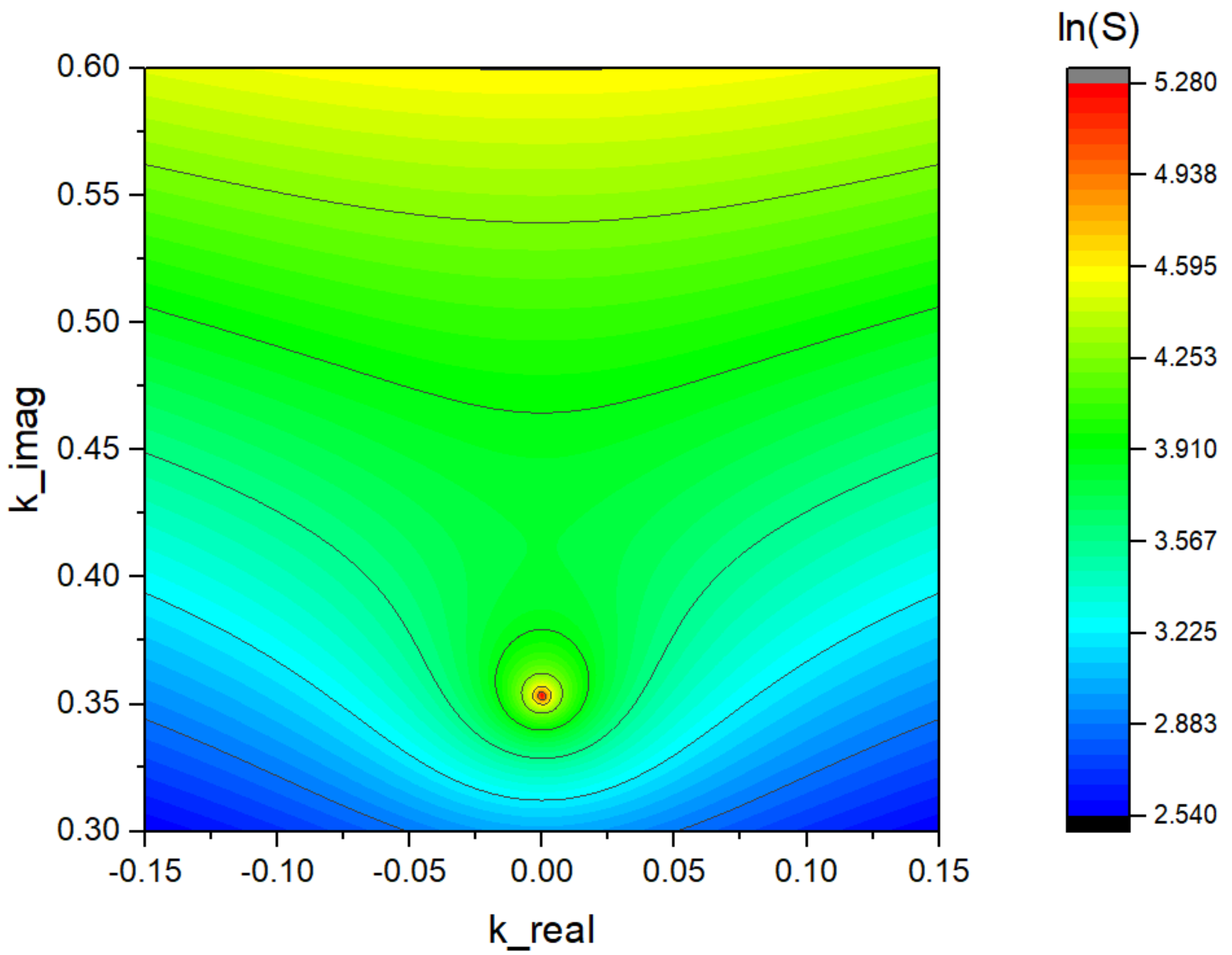
Structure of the S-matrix in the complex k-plane

E =k^2/2··



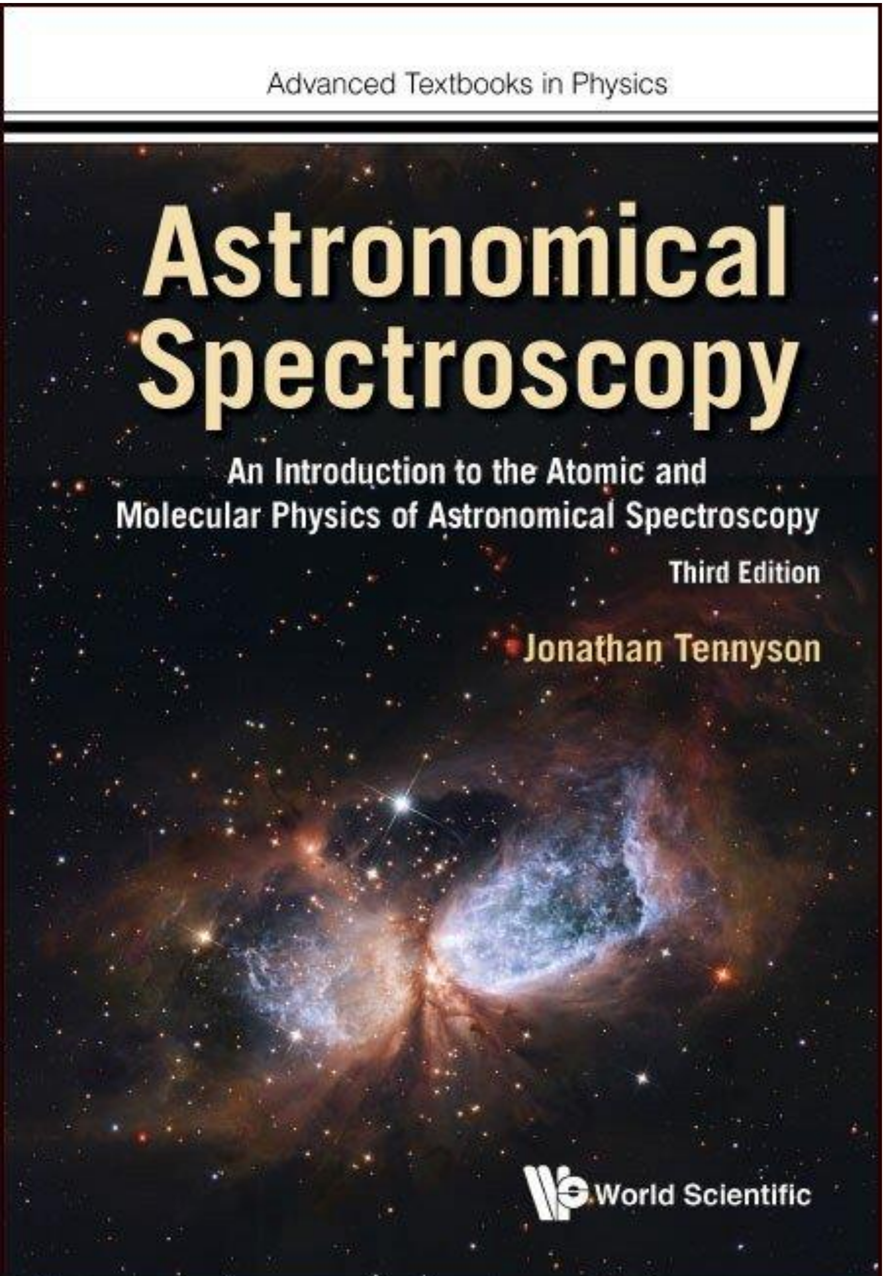
PS Bingham & JD Gorfinkiel,
Reskit: A toolkit to determin the poles of an S-matrix
Computer Phys. Comms. 239 272 (2019)

Ar – Ar bound state as pole in S-matrix in the complex k-plane.



RmatReact: current status

- Ar – Ar elastic collisions: completed
- $O(^3P_J)$ – He inelastic collisions: nearing completion
- Triatomics (DVR3D) development in progress
- Collaboration with Brianna Heazlewood (Oxford) on ultralow energy ion – molecule collisions



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Contemporary Physics (2006)

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