Atomic and molecular suite of R-matrix codes for ultrafast dynamics in strong laser fields and electron/positron scattering

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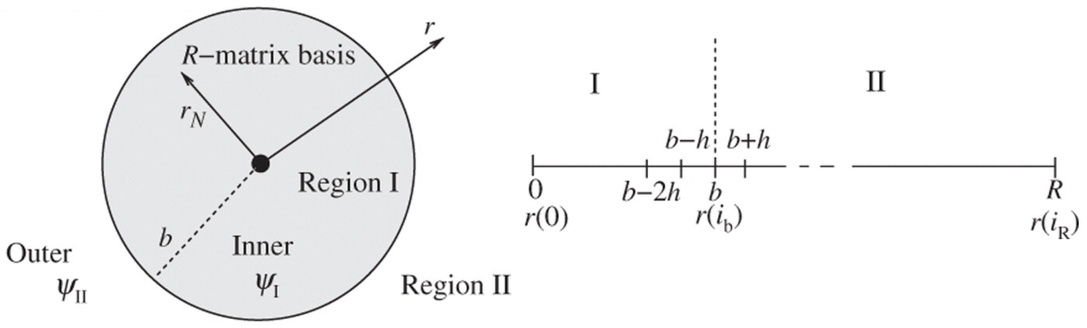
1. Introduction

The R-matrix atomic and molecular suites of codes have recently been upgraded and made available to the community. A set of atomic and the molecular time-independent codes form their core. On the atomic side these are the well-established RMATRXI and RMATRXII codes: both use a B-spline representation of the continuum; RMATRXI allows the inclusion of relativistic (Breit-Pauli) corrections. On the molecular side, a major development has led to the release of UKRmol+ (`https://zenodo.org/l`), based on code originally developed for electron/positron - molecule scattering. This suite has been extended to enable photoionization calculations, to include B-splines in the representation of the continuum and to enable parallel Hamiltonian builds. The second layer of the R-matrix suite comprises R-matrix with time (RMT) codes (`https://gitlab.com/Uk-amor/RMT/rmt`) which can now be used to propagate in time both the atomic and molecular (in the fixed-nuclei approximation) wavefunctions. Recent developments allow the use of arbitrary polarized light and interfacing with the atomic RMATRXI suite thus enabling studies of spin-orbit dynamics for atoms in ultrafast laser fields.

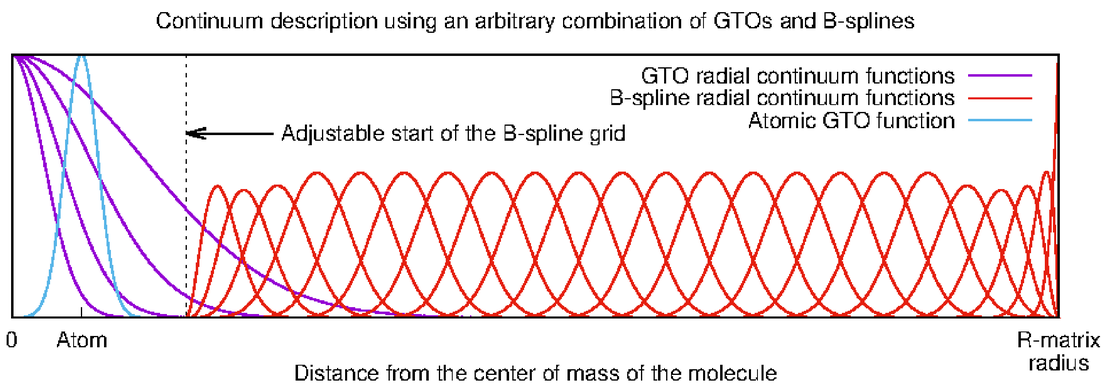
2. R-matrix approach: partitioning of the configuration space



Partition of the configuration space for the electron coordinate. In the **inner region** (I) an eigenstate expansion representation of the wavefunction is chosen, while in the **outer region** (II) a finite-difference representation (RMT) or expansion into orthogonal polynomials (RMATRXI, RMATRXII, UKRmol+) is used. The boundary of region I is at $r = b$ and the outer (asymptotic) boundary of region II is at $r = R$. For a detailed exposition of the theory see [1, 2, 3].

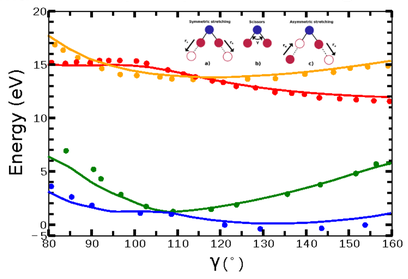
2. Time-independent molecular codes

- Continuum description: GTOs and/or B-splines
- Parallel evaluation of the molecular integrals, optional use of quad precision
- Parallel Hamiltonian build and diagonalization [4]
- Use of pseudostates for modelling of polarization effects

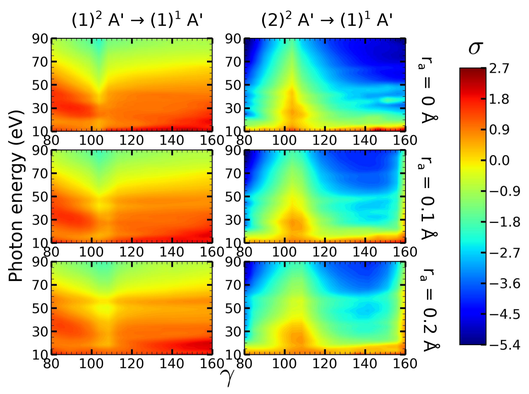


3. Applications: electron-molecule scattering, atomic and molecular photoionization

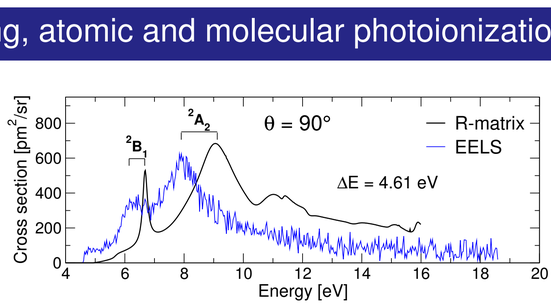
- **Electron collisions with thiophene** [5]: Close-Coupling calculation with 25 states, $L_{max} = 4$, double precision integrals.
- **Photoionization of NO_2** [6, 7]: Close-Coupling model, 192 ionic states, $L_{max} = 6$, 102 geometries, quad precision integrals.
- **Photoionization of CO_2** [8, 9]: Close-Coupling model, 300 ionic states, $L_{max} = 7$, quad precision integrals.



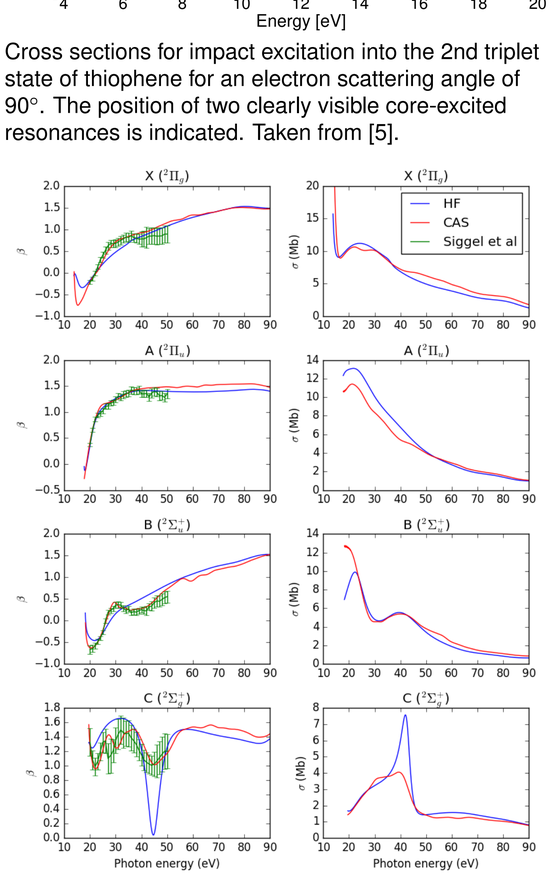
NO_2 potential energy curves ($r_a = 0$) for the $(1)^2A'$ (blue), $(2)^2A'$ (green) neutral and $(1)^3A'$ (orange), $(1)^1A'$ (red) ionic states. Solid lines: R-matrix [7]. Dots: accurate calculations of Hirst (JCP, **115**, 9320, 2001) and Kurkal et al (JCP **119**, 1489, 2003).



NO_2 partial photoionization cross sections (in Mb) in logscale for $80° \leq \gamma \leq 160°$ for the $(1)^1A'$ final ionic state. Taken from [7].



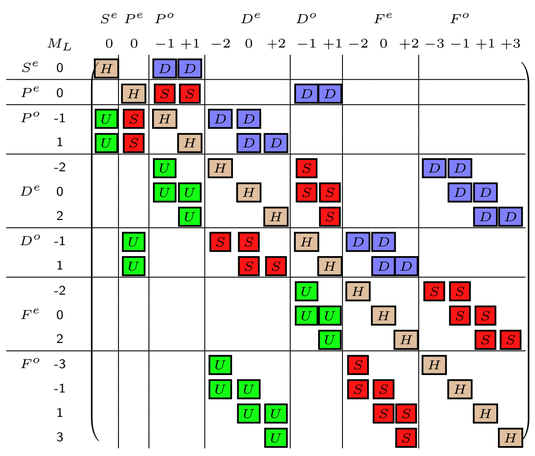
Cross sections for impact excitation into the 2nd triplet state of thiophene for an electron scattering angle of 90°. The position of two clearly visible core-excited resonances is indicated. Taken from [5].



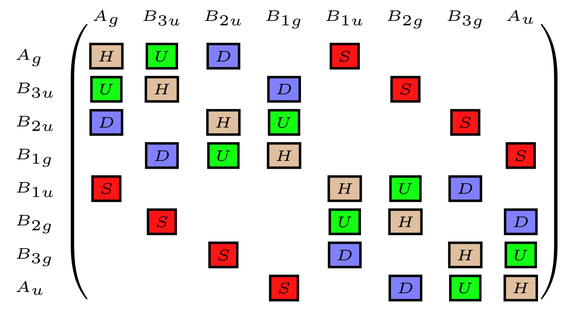
CO_2 partial cross sections in Mb (right column) and β-parameters (left column) for the four ionic states (in rows) as obtained from the HF (blue lines) and CAS-CI (red lines) calculations. The green lines are the experimental values of Siggel et al. Taken from [9].

4. Time-dependent atomic and molecular codes

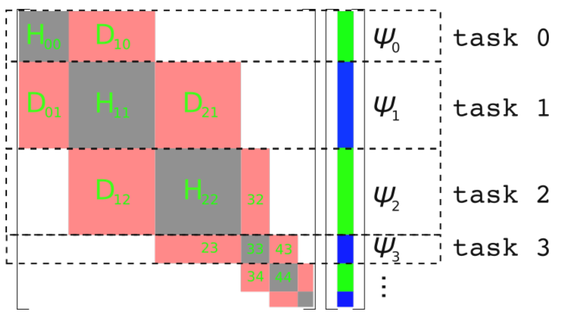
- Recently extended to support **molecular** calculations
- Allows use of an arbitrarily polarized light
- Optional use of the relativistic Breit-Pauli Hamiltonian for atoms
- Advanced MPI/OpenMP parallelization scheme



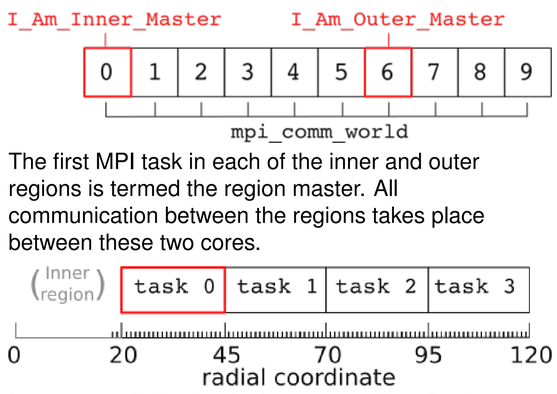
Atomic inner-region Hamiltonian for ***S***, ***P***, ***D*** and ***F*** symmetries, accessible for xy-plane polarization, assuming an S^e initial state.



Inner-region Hamiltonian for the case of a molecule belonging to the D_{2h} point group and electric field having all three (x, y, z) components non-zero. Dipole blocks labelled ***D***, ***S*** and ***U*** indicate dipole transitions induced by the x, y, z field components respectively.



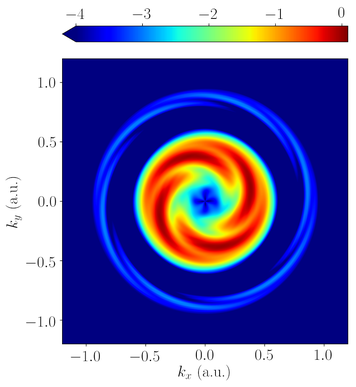
Layer 1 parallelism in the inner region. The Hamiltonian matrix and wavefunction vector are divided into symmetry blocks, with each block assigned to (at least one) MPI task. Layer 2 parallelism consists in subdividing rows in each block among a set of MPI tasks assigned to that block.



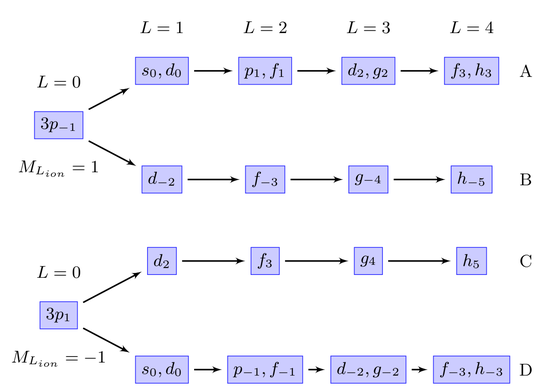
The first MPI task in each of the inner and outer regions is termed the region master. All communication between the regions takes place between these two cores.

Layer 1 parallelization in the outer region. Each outer-region MPI task handles a subset of the entire physical space. Communication is only required between nearest neighbours.

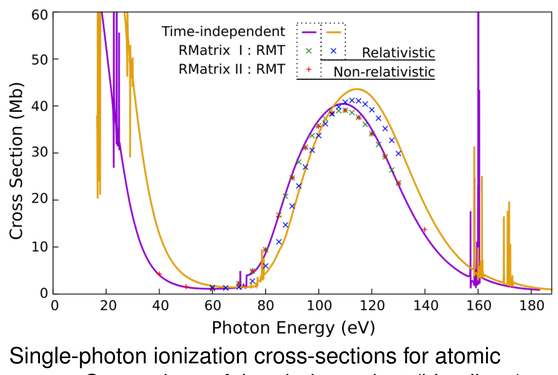
5. Applications: electron vortices, perturbative atomic and molecular dynamics



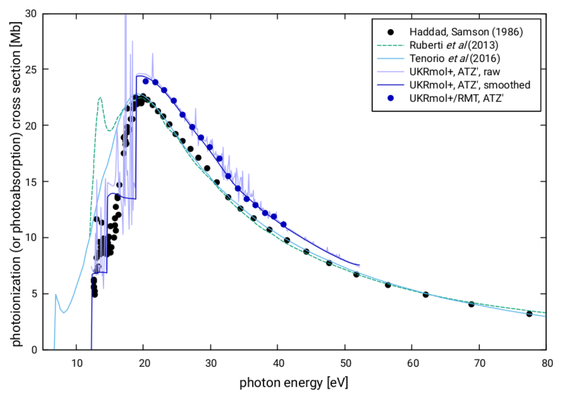
Photoelectron momentum distribution for Ar, irradiated by a pair of counter-rotating, circularly polarized, 6-cycle, 9-eV, 5×10^{13} W.cm^{-2} laser pulses. Taken from [3].



Pathways for ionization of Ar **3*p*** electrons by a pair of counter-rotating, circularly polarized pulses. Taken from [3].



Single-photon ionization cross-sections for atomic xenon. Comparison of time-independent (blue lines) and time-dependent (blue points) R-matrix approaches. RMT parameters: 3 cycles ramp-on, 6 cycles at maximum intensity and 3 cycles ramp-off of peak intensity 0.13×10^{14} W.cm^{-2}. Taken from [3].



Single-photon ionization cross-sections for H_2O. Results of time-independent (solid lines) and time-dependent (individual points) calculations. Model: aug-cc-pVTZ, CAS(8,10), $L_{max} = 7$. RMT parameters: 200 cycles, $I = 10^{10} W.cm^{-2}$.

6. References

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