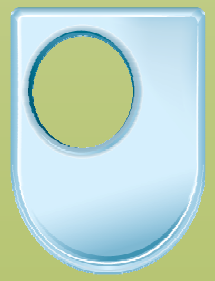
UK R–matrix Atomic and Molecular Physics HPC Code Development Project



The Open University

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UK-RAMP

UK R-matrix Atomic and Molecular Physics HPC Code Development Project

A collaboration between QUB, OU, UCL and Daresbury

The development of a set of high-quality, developer- and user-friendly, atomic and molecular HPC codes addressing important newly-emerging areas of Science (e.g. Atto-second Science, biological radiation damage phenomena) where a detailed understanding of multi-electron dynamics in atoms and molecules is known to be crucial but is so far largely lacking.

The training of a cohort of people with expertise in HPC code development to help build a critical mass of such expertise in the UK academic community.

UK-RAMP: science

- Atoms and molecules in IR/visible/UV and XUV intense laser fields:

single- and double-ionization, rescattering-induced double-ionization interaction of coherent x-rays (FEL) with K-shell electrons of matter, high-harmonic generation, Attosecond science

- Electron (and positron) scattering from molecules

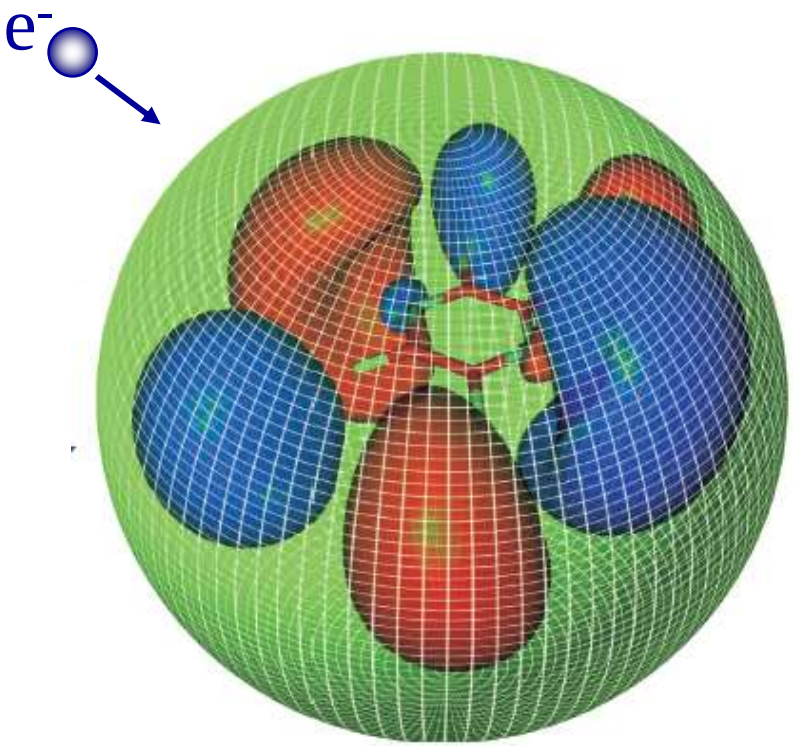
  - Plasma Physics and plasma processing
  - Atmospheric & Interstellar Models
  - Radiation Physics & Chemistry
  - Radiobiology
  - Single-molecule engineering
  - Laser Physics
  - Exo-biology (a.k.a. Astrobiology)

The R-matrix method

The R-matrix method

- Developed initially for nuclear physics
- Extensively used for electron-atom collisions: 70s onwards, consistent software development (Daresbury)
- More recent development for molecular targets (80s diatomics and 90s poliatomics; Daresbury, UCL, Royal Holloway); particularly suitably to treat electronically inelastic processes
- Also used to study photoionization, photorecombination, atoms in fields, multiphoton processes (R-matrix Floquet method for long pulses and TD methods for short pulses; QUB)
- Electron interactions with solids

R-matrix method



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

(within the Fixed-Nuclei approximation)

Inner region:

- exchange and correlation important
- multicentre expansion of Ψ
- adapt quantum chemistry techniques $\Rightarrow$ computer requirements shoot up as number of e^- increases.

Outer region:

- exchange and correlation are negligible
- long-range multipolar interactions sufficient
- single centre expansion of Ψ

P. Burke, R-matrix theory of Atomic Collisions (Springer Series on Atomic, Optical, and Plasma Physics, 2011).

R-matrix method

1. calculation of target properties: electronic energies and wavefunctions (for transition moments)

2. inner region: calculation of Ψ_k^{N+1} from diagonalization of $\mathbf{H}^{N+1}$

$$\Psi_k^{N+1} = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_j b_{j,k} \phi_j^{N+1}$$

3. outer region: match channels at the boundary and propagate the R-matrix to the asymptotic limit where analytical solutions are available

$$R_{ij}(a,E) = \frac{1}{2a} \sum_{k=1} \frac{w_{ik}(a) w_{jk}(a)}{(E_k - E)} \qquad w_{ik}(a) = \left\langle \phi_i^N Y_{l_i m_i} \middle| \Psi_k^{N+1} \right\rangle$$

The aims of the project

UK-RAMP

Initial set of codes:

- **HELIUM**: solves the two-electron TDSE to describe response of an atom/molecule to intense laser light on the femto/atto scale; *ab initio*, full-dimensional. Running very efficiently over > 8,000 cores on HECToR).
- An adapted version of **RMATRIXII/RM95** (a time-independent atomic R-matrix multi-electron code) incorporating B-spline basis functions and dipole matrix elements.
- **PFARM**: a parallel implementation of the Flexible Asymptotic R-Matrix (FARM) code used for huge time-independent atomic Outer Region problems (on HECToR, etc.)
- **UK-Molecular R-matrix suite**: computing electron (and positron) molecule collision processes. Largely used in single processor mode even though some runs currently take months; developed with CCP2 support over ≈ 30 years.

UK-RAMP

Codes we promised:

- **UKRMol**: re-engineered, parallel version of the UK Molecular R-matrix suite.
- **MPFARM**: implementation Outer Region time-independent code PFARM for both atoms and molecules to enable the treatment of massive Outer Region problems
- **RMT**: time-dependent
    - **TD-RA**: Atomic Inner Region based on the adapted **RMATRIXII/RM95**
    - **TD-UKRMol**: version of UKRMol
    - **TD-OUTER** Outer Region code dealing with the interaction of a single electron with an intense laser field.
- **TD-UKRMol+:** advanced version of TD-UKRMol operating over an extended energy range using completely revised basis sets for the Inner Region problem.
- **TD-2eOUTER**: new Outer Region code using HELIUM methods to handle two-electrons.
- **TD-RA2e**: prototype version of a TD Inner Region atomic code which will treat problems involving two electrons in the continuum for complex atoms.

What we set out to do

- Develop codes for specific applications
- Do things properly:
  - Version control
  - Systematic testing
  - Coding standards
  - Communication between developers
  - Feedback from users (bug reporting)
  - Portability
  - Maintainability

Main issues

CCPForge:

http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-in/

http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-out/

- Social problem more difficult to resolve than technical: high turnover, lack of interest, ‘what’s in it for me?’, …
- Lack of documentation made it impossible to modify some codes: complete re-write?
- Limited experience of developing software for HPC environments

Nature **467**, 775-777 (2010)
Nature **482,** 485–488 (2012)

The UKRmol suite

The UKRmol suite before UK-RAMP

- Used in the UK (UCL, OU, QUB) and abroad (France, Japan, Germany, US….)
- Based on older codes (Burke, Noble, etc…+ Almölf and Taylor)
- Sort of Fortran90, but not completely
- Completely serial
- No consistent update strategy (*ad hoc* modifications when required for research)
- No version control (e.g: old/ , oldest/, etc..)
- No detailed record of changes
- No proper documentation (still a problem)

What we couldn't do and why

- Treat targets with many electrons > 30/40
- Include many pseudostates to describe near threshold ionization and polarization effects (essential for e^+-scattering)

$\mathbf{H}^{N+1}$ matrix too big and/or outer region too slow

- Treat many-e^-, low-symmetry targets

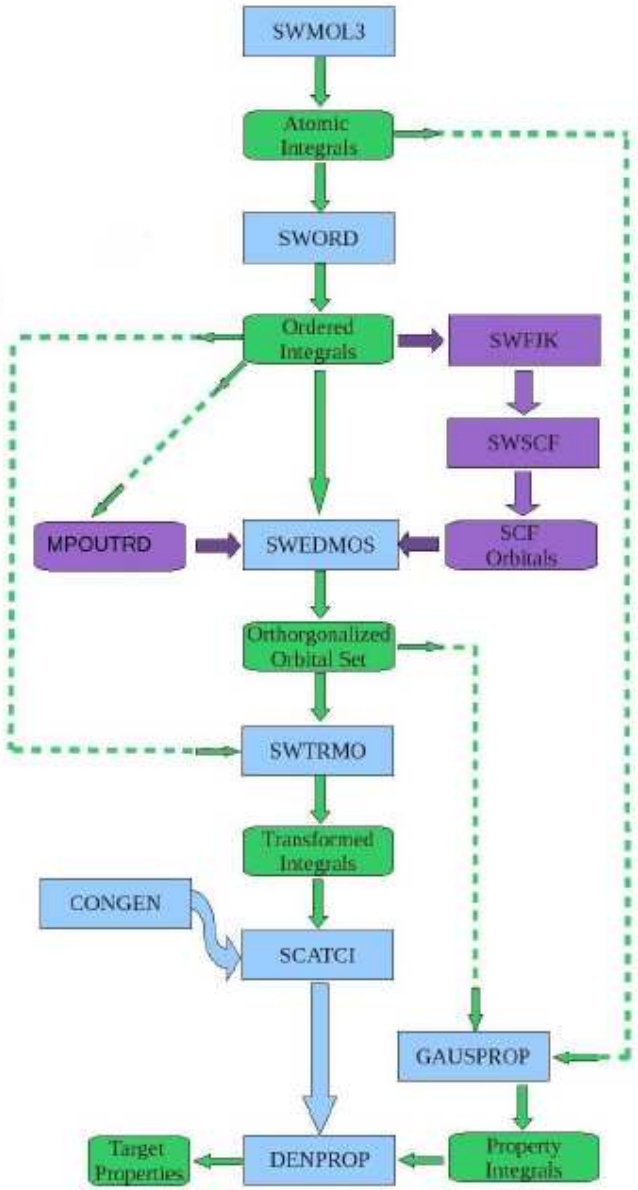
Integral reordering requires too much memory (> 48Gb)

- Describe Rydberg states

R-matrix sphere too small

UKRMol-in: target run

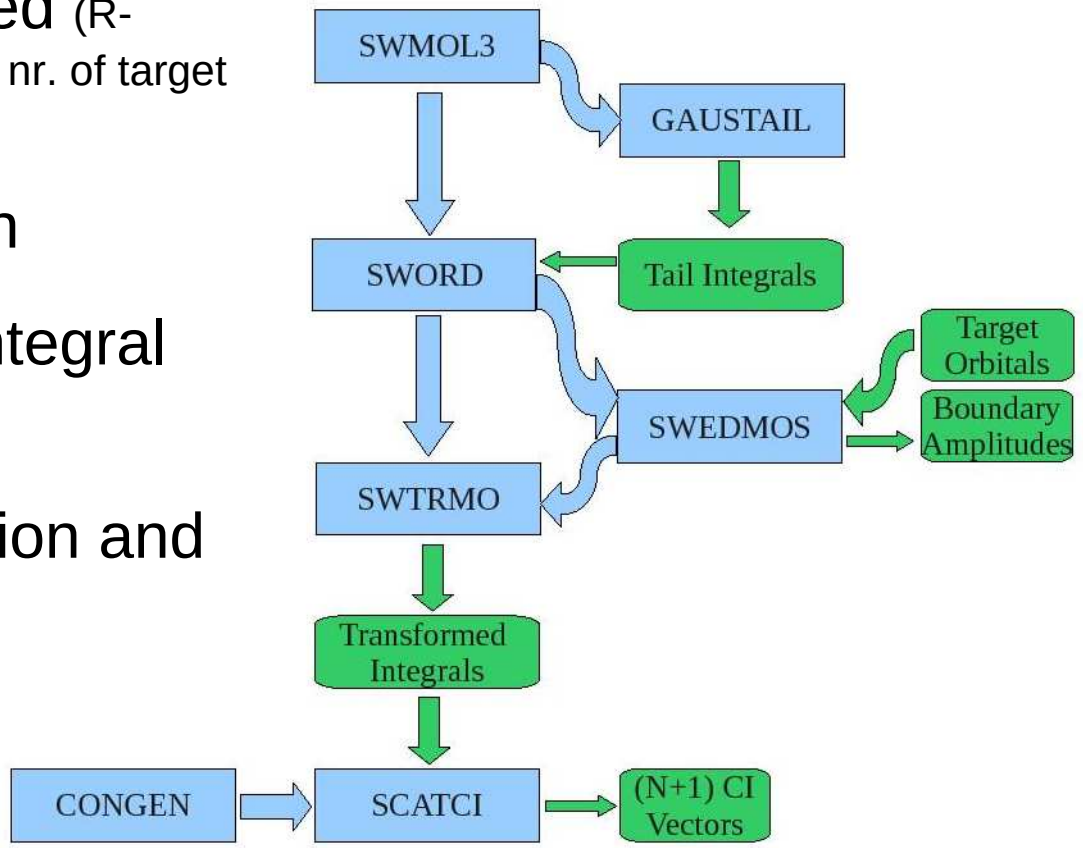
- Quantum Chemistry input needed (molecular geometry, point group, basis set, CI model)
- **Not** computationally demanding
- Some or all replaced by standard QC codes (MOLPRO)



Important: accurate permanent dipole moments and excitation thresholds

UKRmol-in: inner region run

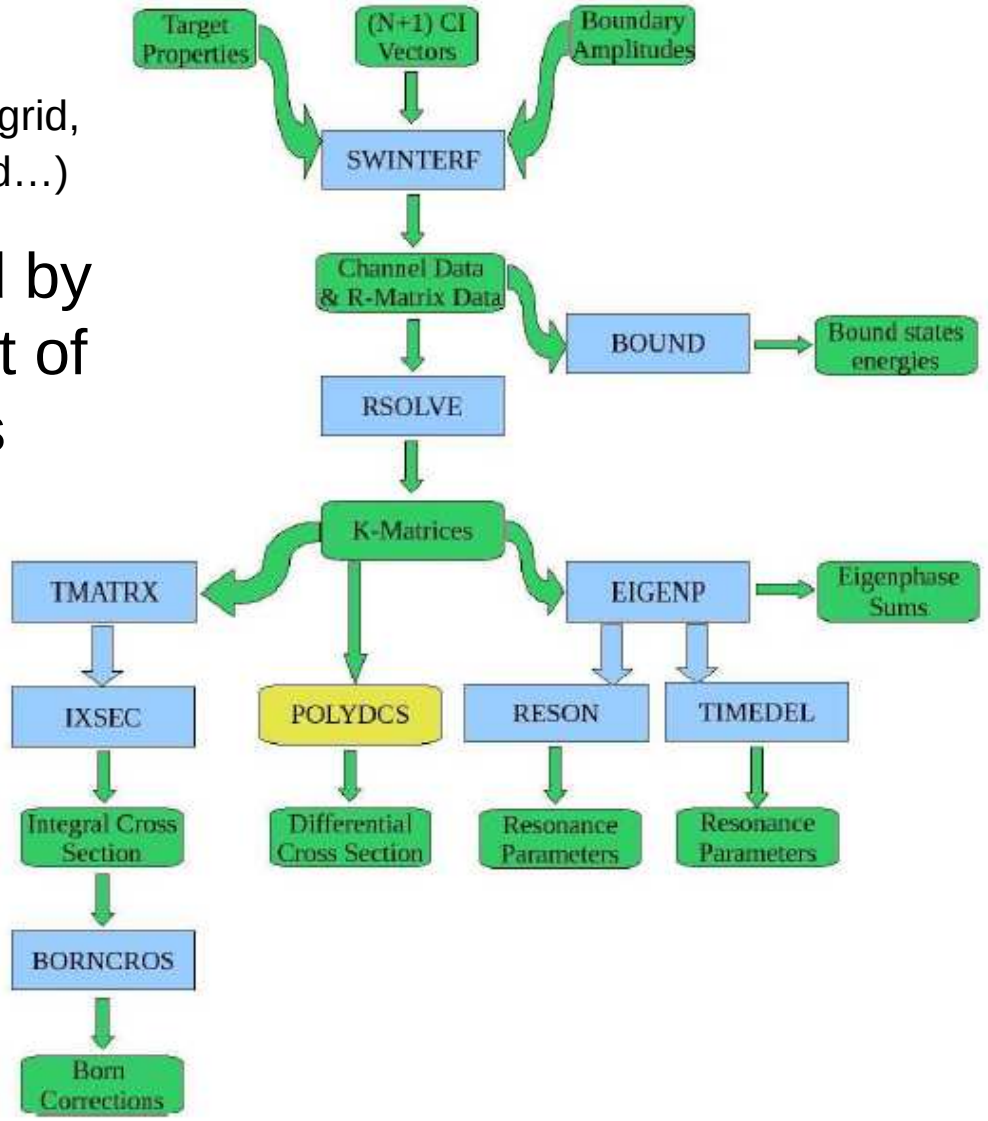
- Scattering input needed (R-matrix radius, continuum basis set, nr. of target states, …)
- Integral transformation
- Memory handling in integral reordering
- Hamiltonian construction and diagonalization



Important: no-leak outside the inner region and description of polarization

UKRmol-out

- Scattering input needed (E grid, interaction potential, observables required…)
- Propagation step (required by several modules): solves set of couple differential equations using matrix diagonalization



Developments

- UKRmol-in now compliant with Fortran95 standard
- Modularization/abstraction for global data and global procedures
- Global treatment of the precision
- High level routines now call low-level subprograms via wrapping routines
- Interface with MOLPRO (Molden) now part of the suite
- OpenMP implementation of the Hamilonian diagonalization

J. M. Carr *et al.,* Recent developments in UKRmol, *Eur. Phys. J.* D., 66:1–11, 2012

Partitioned R-matrix

If the H^{N+1} matrix is very big (> 10^5 x 10^5) it is not practicable to determine all eigenpairs. The **partitioned R-matrix method** allows to generate the R-matrix using only m roots:

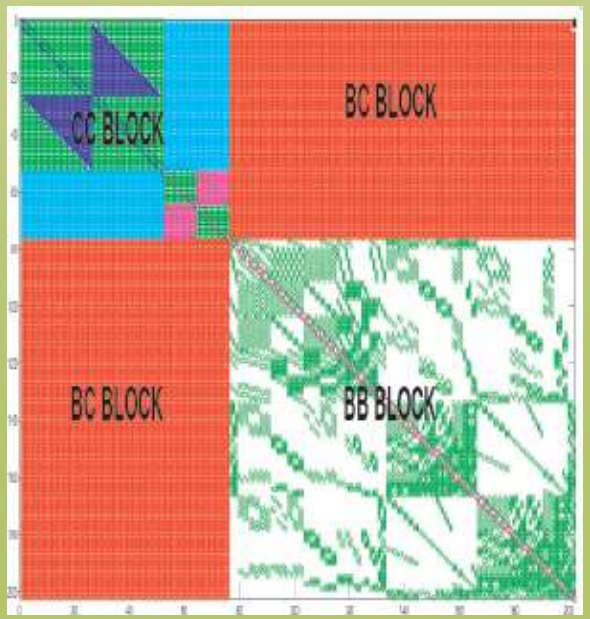
$$R_{ij}(a,E) = \frac{1}{2}\sum_{k=1}^{m} w_{ik}(a)\,w_{jk}(a)\left(\frac{1}{E_k - E} - \frac{1}{E_0 - E}\right) + \delta_{ij}\left(\frac{s_i}{E_0 - E} + R_i^C\right).$$

$m/M \approx 5\text{-}10\%$

Efficient techniques for parallelizing the diagonalization of sparse matrices can be implemented

MPI build and diagonalization

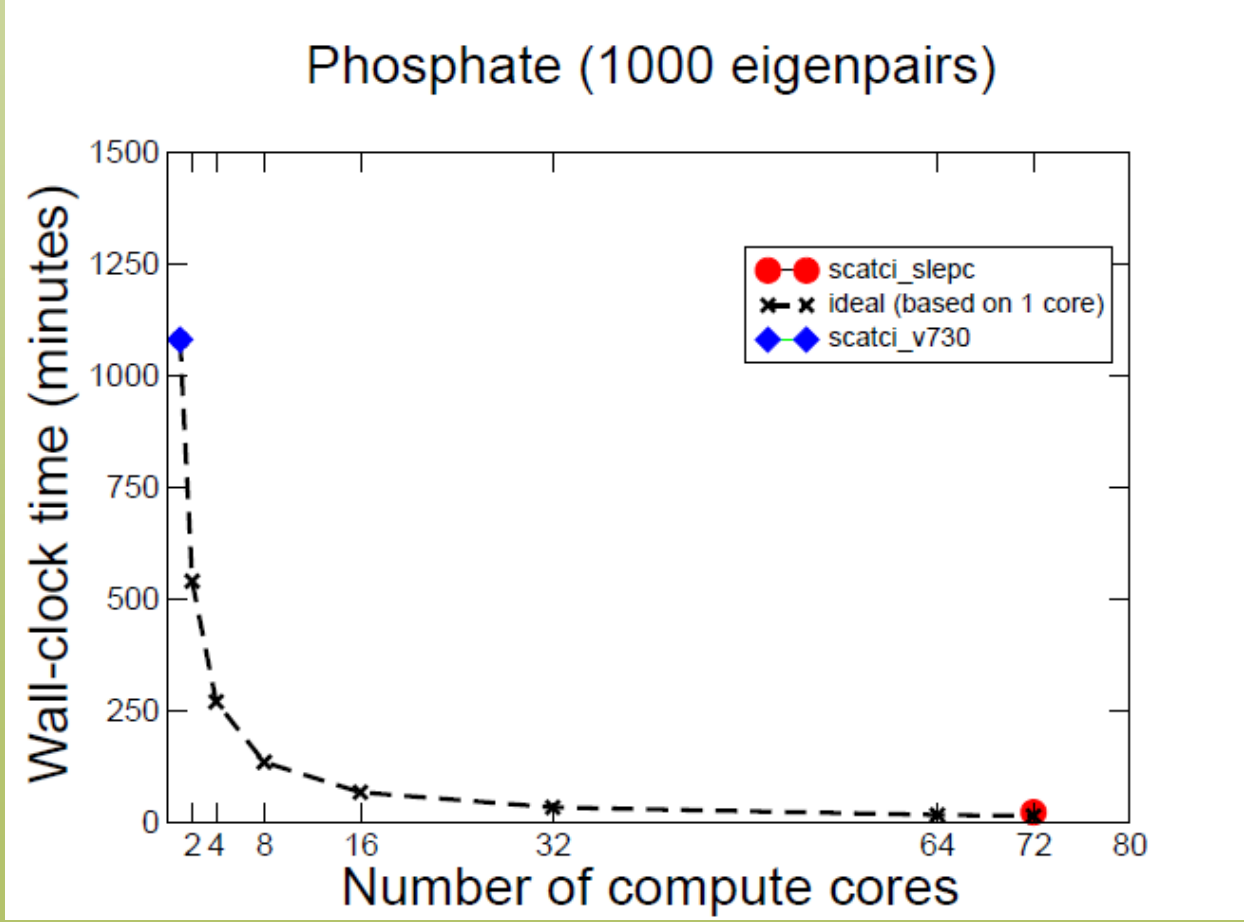
- H is highly sparse (> 95%)
- Using a “partitioned” R-matrix method, only ~ 5-10% of eigenpairs are required
- OpenMP version currently available: uses arpack (a variant of the Lanczos method dealing with real symmetric matrices)
- MPI version currently in development: uses PETSc and SLEPc (Scalable Library for Eigenvalue Problem) available on HECToR
- Only way to load-balance is to know about BB structure before diagonalization stage: initial sweep to determine the number of non-zeros element in each row.
- Parallelized build too; Hamiltonian no longer saved to disk but distributed to nodes



The form of H

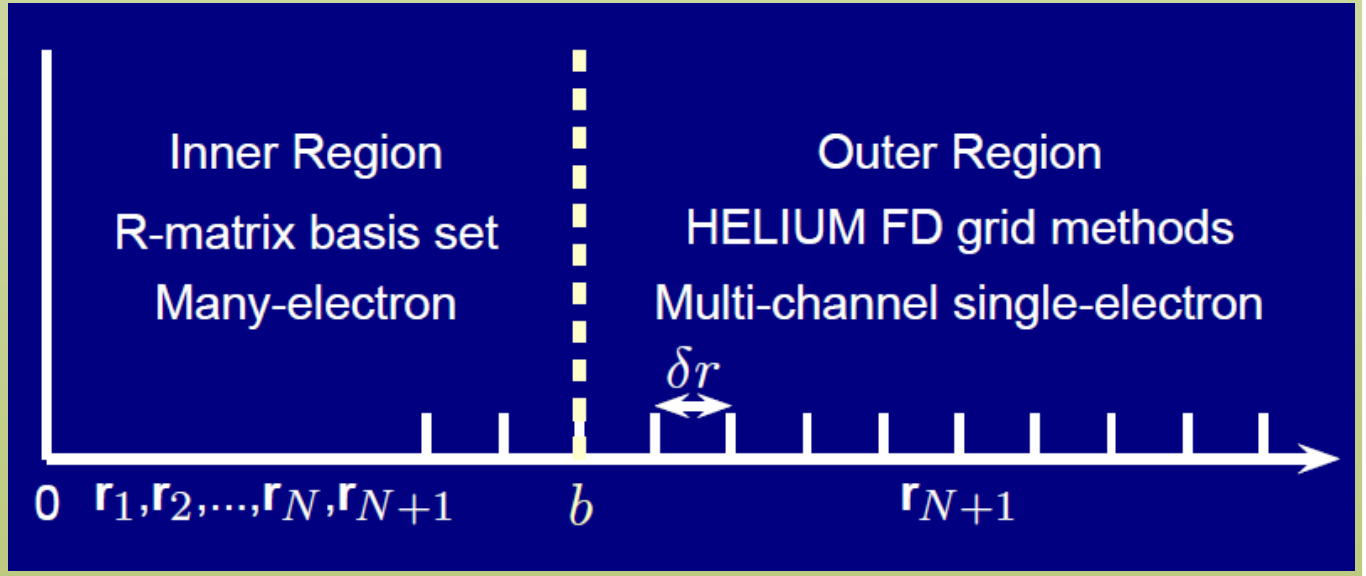
H diagonalization

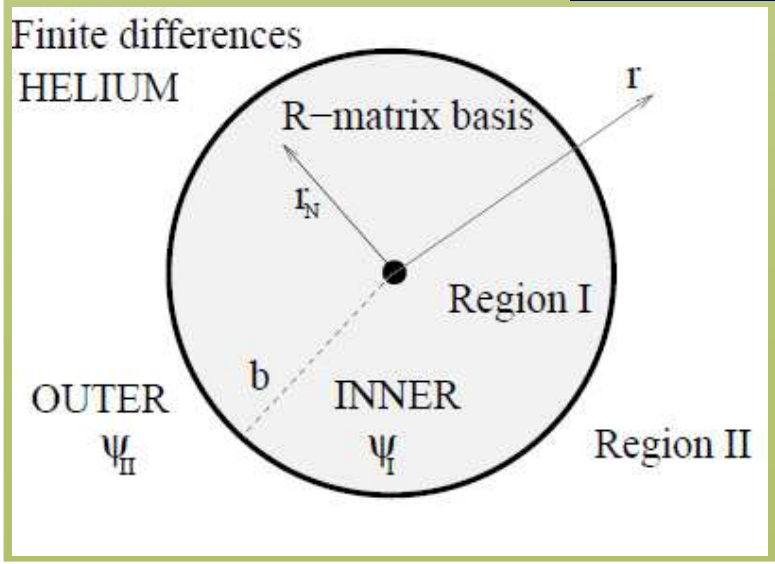
- Test with H dimension ~ 120000 and 1% non-zero elements



UK-RAMP

RMT: multi-electron inner region and a one-electron outer region; TDSE in both regions. Working for atomic case and in progress for molecular one.





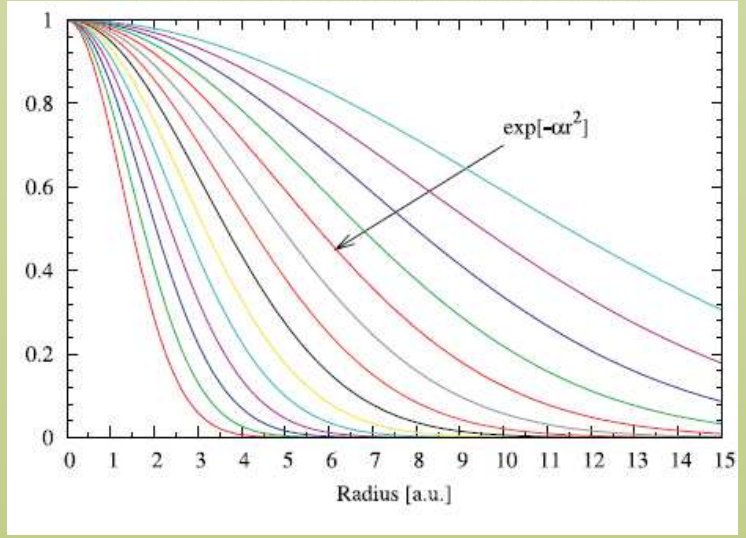
LAA Nikolopoulos, JS Parker and KT Taylor 2008 *Phys. Rev.* A 78 063420; LR Moore, MA Lysaght, LAA Nikolopoulos, JS Parker, HW van der Hart and KT Taylor, *J. Mod. Opt.* 2011

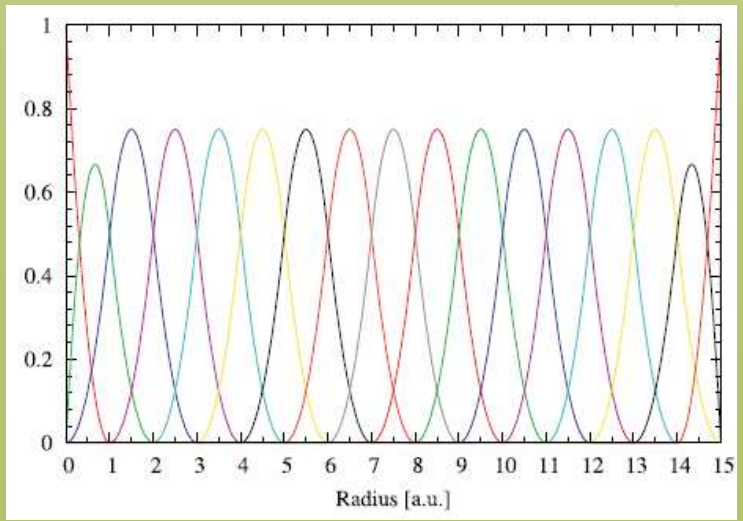
Work in progress

- Handling of integral sorting (to avoid > 48Gb memory requirement) in UK-Rmol
- Inclusion of time-dependence in molecular inner region in progress (TD-UKRmol)
- Handling 2 e^- in the continuum (TD-2e)
- TD-UKRMol+

Work in progress: TD-UKRmol+

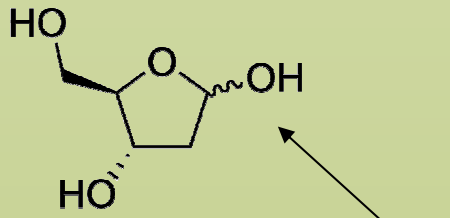
- Gaussian type orbitals for the continuum no longer a good idea
- Use numerical functions: B-splines
- Numerical integration
- Evaluation of the overlap integrals between real spherical GTOs and B-spline orbitals
- Complete re-write of several of the programs in the suite





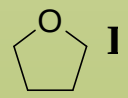
What we can now do

DNA

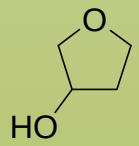


deoxyribose

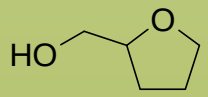
tetrahydrofuran (THF)



I

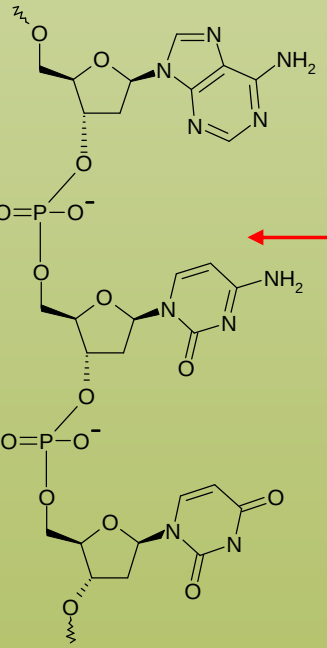


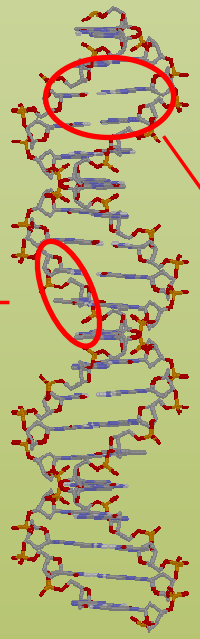
II



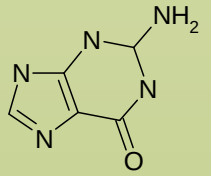
III

+ H_2O

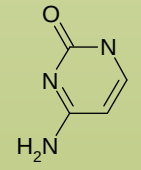




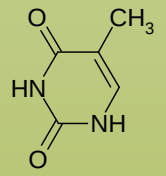
Guanine



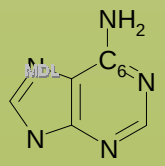
Cytosine



Thymine



Adenine



and .....

- Electronic excitation of DNA bases including guanine and adenine
- $e^+ + C_2H_2$: with pseudostates
- $e^- + CH_4$: with pseudostates
- $e^- + CH^+$:resonances using pseudostates
- $e^- + C_4H_4N_2$: systematic use of MOLPRO data

Conclusions and outlook

- Some work still to do to get UKRmol up to scratch
- More work to do to have the photon codes ready
- Long term prospects? (CCPQ)
- Strengthen user and developer community
- Formalise release process…

Acknowledgements

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UK Molecular R-matrix Project:

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