Time-dependent R-matrix theory

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Goal

- Improve our understanding of fundamental dynamics underlying basic processes
- Most systems are inherently multi-electron systems
- Gain understanding of role of multi-electron dynamics within atoms/molecules

Goal

- Multi-electron systems have many degrees of freedom (3 per particle)
- Large-scale computation possible for two electrons
- What about systems with more than two electrons that can respond to the field?
- Need to consider effective approximations

R-matrix theory

- R-matrix theory was developed in the late 40's as a phenomenological method to study nuclear scattering processes

- For these processes, space could be separated:
  - an inner region within which little was known
  - an outer region with good approximate wavefunctions
  - Scattering processes can be described by a phenomenological R-matrix at the boundary, which links these outer-region wavefunctions

- It was recognised in the 50s that this phenomenological approach could be used as an ab-initio approach for atomic scattering processes

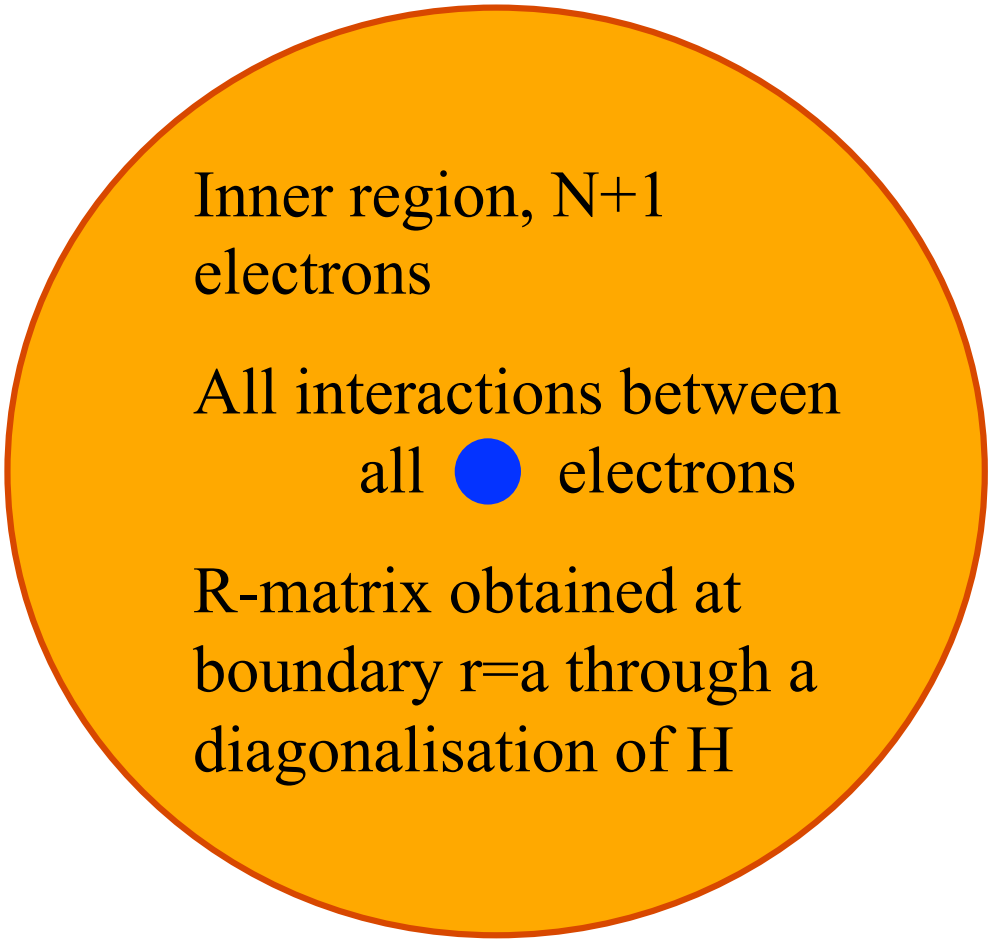
Textbook

- P.G. Burke
  R-matrix theory of atomic collisions (2011)
  Springer series on atomic, optical and plasma physics 61

- Includes, in addition to collisions,
  photoionization,
  R-matrix-Floquet theory for long pulses,
  Time-dependent R-matrix theory
  (PRA 79, 053411 is better on TDRM)

- Does not include:
  ultra-cold atom-atom collisions

Basics of R-matrix theory



Outer region, 1 electron

Electron feels long-range field

Propagation of the R-matrix

match R-matrix to asymptotic solutions at a distance a'

R-matrix theory

- Multi-electron systems substantially more complicated than single-electron systems
- Notation can obscure maths/physics
- Combine basic ingredients first
  Develop extra features later
- Elastic potential scattering (single electron)

R-matrix theory

- The starting point is the (radial) Schrödinger equation

$$H\psi = E\psi$$

- This equation must be solved separately for the inner region and the outer region.
  The two solutions must then be linked together.

- We start with the inner region.

- Consider radial wavefunctions of form $\psi(r)/r$

Inner region

- The Hamiltonian is not Hermitian within the inner region
- Physically: an ionization process involves flow from inner region to outer region
  → norm of ψ in inner region not conserved
- Mathematically: the kinetic energy operator is not Hermitian

$$\int_0^a \psi_1^*(r)\frac{d^2}{dr^2}\psi_2(r)dr = \int_0^a \left(\frac{d^2}{dr^2}\psi_1^*(r)\right)\psi_2(r)dr +$$

$$+\left[\psi_1^*(r)\frac{d}{dr}\psi_2(r)\right]_0^a - \left[\left(\frac{d}{dr}\psi_1^*(r)\right)\psi_2(r)\right]_0^a$$

Inner region

- Reordering the equation as

$$\int_0^a \psi_1^*(r)\frac{d^2}{dr^2}\psi_2(r)dr \; - \; \left[\psi_1^*(r)\frac{d}{dr}\psi_2(r)\right]_0^a =$$

$$\int_0^a \left(\frac{d^2}{dr^2}\psi_1^*(r)\right)\psi_2(r)dr - \left[\left(\frac{d}{dr}\psi_1^*(r)\right)\psi_2(r)\right]_0^a$$

shows that the operator

$$\frac{d^2}{dr^2} - \delta(r-a)\frac{d}{dr}$$

is Hermitian (radial Ψ includes term r$\rightarrow$ Ψ(0)=0)

Inner region

- The potential energy is a function of r, and thus Hermitian
- The angular kinetic energy is Hermitian
- The radial kinetic energy can be made Hermitian as

$$-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\delta(r-a)\frac{d}{dr}$$

Inner region

- The radial Schrödinger equation is then rewritten as

$$\left(H + L_b - E\right)\psi = L_b\psi$$

$$L_b = \frac{1}{2}\delta(r-a)\frac{d}{dr}$$

so that the operator on the LHS is Hermitian.

- Obtain the eigenvalues and eigenvectors of $H+L_b$ in an appropriate eigenbasis

- With L_b included, basis can contain functions with $\psi(a)\neq 0$, $\psi'(a)\neq 0$. Essential for TDRM!

Inner region

- Let us have eigenvalues E_k and associated eigenfunctions $|\Psi_k\rangle$. Then

$$
\begin{aligned}
|\psi\rangle &= (H + L_b - E)^{-1} L_b |\psi\rangle \\
&= \sum_k (H + L_b - E)^{-1} |\psi_k\rangle\langle\psi_k| L_b |\psi\rangle \\
&= \sum_k (E_k - E)^{-1} |\psi_k\rangle\langle\psi_k| L_b |\psi\rangle \\
&= \sum_k \frac{1}{2(E_k - E)} |\psi_k\rangle\langle\psi_k| \delta(r-a) \frac{d}{dr} |\psi\rangle \\
&= \sum_k |\psi_k\rangle \frac{1}{2(E_k - E)} \left(\psi_k(a) \frac{d}{dr} \psi \Big|_{r=a} \right)
\end{aligned}
$$

Inner region

- The final result of this manipulation gives

$$|\psi\rangle = \sum_k |\psi_k\rangle \frac{1}{2(E_k - E)} \left(\psi_k(a) \frac{d}{dr} \psi \Big|_{r=a} \right)$$

which shows that the wavefunction in the inner region is determined entirely by its derivative at the boundary and the energy.

Inner region R-matrix

- Now we can look at what happens at the boundary. So we evaluate Ψ on the LHS at the boundary, while on the RHS we evaluate Ψ_k.

  With R the so-called R-matrix, this gives

$$\psi(a) = \sum_k \psi_k(a) \frac{1}{2(E_k - E)} \psi_k(a) \left(\frac{d}{dr} \psi \right) \Bigg|_{r=a}$$

$$= R \left(\frac{d}{dr} \psi \right) \Bigg|_{r=a}$$

Inner region R-matrix

$$\psi(a) = \sum_k \psi_k(a) \frac{1}{2(E_k - E)} \psi_k(a) \left(\frac{d}{dr} \psi \right) \Bigg|_{r=a}$$

$$= R \left(\frac{d}{dr} \psi \right) \Bigg|_{r=a}$$

- This relationship expresses the wavefunction at the boundary in terms of its derivative.
- If it holds at the boundary, it must not only apply to the inner region… it must also apply to the outer region.

Outer region

- In the outer region, the wavefunction is given in terms of asymptotic wavefunctions.

- In an elastic scattering problem, the standard radial wavefunction is of the form

$$\psi = A\left(\psi_{in} - \psi_{out} S\right)$$

with A: overall normalisation
Ψ_{in}, Ψ_{out}: incoming/outgoing wavefunction
S: scattering S-matrix

Details of Ψ_{in}, Ψ_{out} depend on nature of problem

Outer region

- Now substitute outer region wavefunction into equation obtained earlier:

$$A\left(\psi_{in}(a) - \psi_{out}(a)S\right) = RA\left(\psi_{in}'(a) - \psi_{out}'(a)S\right)$$

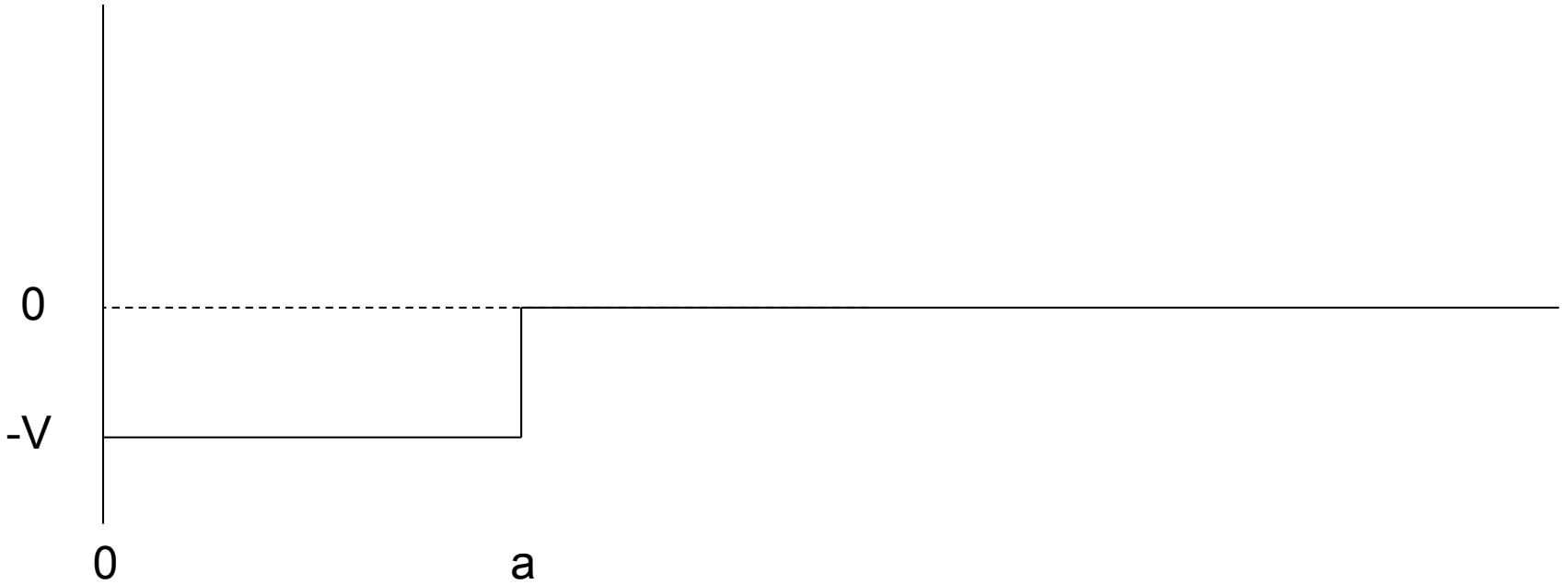
$$\left[\psi_{in}(a) - R\psi_{in}'(a)\right] = \left[\psi_{out}(a) - R\psi_{out}'(a)\right]S$$

$$S = \left[\psi_{out}(a) - R\psi_{out}'(a)\right]^{-1}\left[\psi_{in}(a) - R\psi_{in}'(a)\right]$$

- So by this substitution, we can obtain the S-matrix by straightforward algebra, and hence obtain all the information about the scattering process

Basic application

- Previous outline gives basic principle of R-matrix theory
- Can be used for s-wave scattering off a square-well potential (s-wave: Bessel functions → sin, -cos)

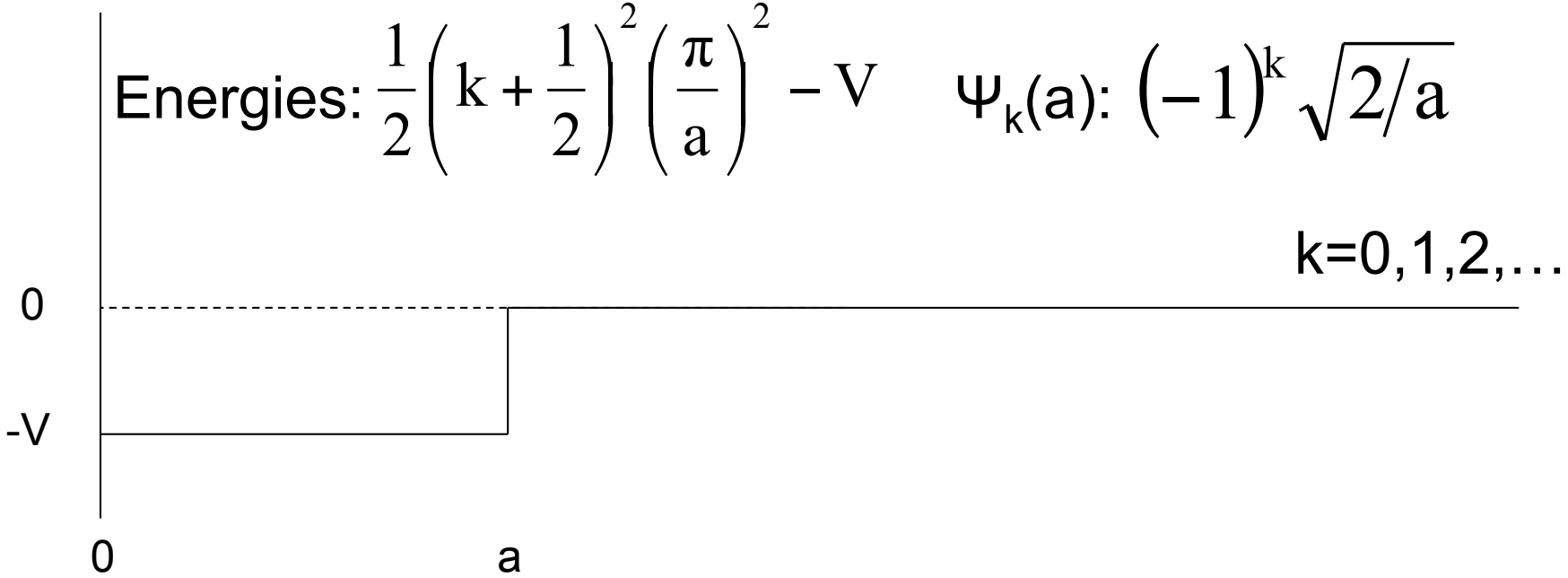


Basic application

- Obtain eigenvalues and eigenfunctions of $H+L_b$.
- Eigenfunctions associate with constant potential in box. Boundary conditions: $\Psi(0)=0$, $\Psi'(a)=0$.

Energies: $\frac{1}{2}\left(k+\frac{1}{2}\right)^2\left(\frac{\pi}{a}\right)^2 - V$ $\Psi_k(a)$: $(-1)^k\sqrt{2/a}$

k=0,1,2,…



Basic application

- We can now use these energies and boundary amplitudes to create the R-matrix at a specific scattering energy E (=$k^2/2$):

$$R = \sum_j \psi_j(a) \frac{1}{2(E_j - E)} \psi_j(a)$$

and then the S-matrix can be obtained as

$$S = \left[e^{ika} - iRke^{ika}\right]^{-1}\left[e^{-ika} + iRke^{-ika}\right]$$
$$= \left[1 - iRk\right]^{-1}\left[1 + iRk\right]e^{-2ika}$$

Basic application

- This is a procedure to explain how to obtain the S-matrix, it is not standard procedure!
- Normally, one uses regular and irregular asymptotic solutions to obtain the K-matrix.
  - This avoids complex arithmetic.
  - Relation between K-matrix and S-matrix $$S = \frac{1 + iK}{1 - iK}$$
- You can calculate the R-matrix yourself from the given eigenvalues and boundary amplitudes. Incoming wavefunction: e^{-ikr}, and outgoing e^{ikr}. (Again,1/r factored out throughout).
- This problem can be solved analytically. $$R = \frac{\tan\left(\sqrt{2(E+V)}a\right)}{\sqrt{2(E+V)}}$$

Further issues

- Atomic multi-channel scattering
  - Several emission routes for electron
  - Inner region wavefunction basis
  - Presence of closed channels
- Accuracy of outer region wavefunctions
  - R-matrix propagation
  - Asymptotic expansion of wavefunction
- Time-dependence

Atomic multi-channel scattering

- Inner-region wavefunction notation not obvious. Obscures basic principles of R-matrix theory

- Wavefunction based on close-coupling expansion
  - Scattering target state has N electrons
  - Total system has N+1 electrons
  - Electron entering outer region is electron N+1
  - Full coordinates X_1: r_1 (radial), θ_1, φ_1 (angular), σ_1 (spin).

$$\psi_{jE}^{\Gamma} = \mathscr{A}\sum_{i=1}^{n} \varphi_i^{\Gamma}(X_N; \hat{r}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} F_{ij}^{\Gamma}(r_{N+1})$$

$$+ \sum_{i=1}^{n} \chi_i^{\Gamma}(X_{N+1}) c_{ij}^{\Gamma}$$

Atomic multi-channel scattering

$$\psi_{jE}^{\Gamma} = \mathscr{A}\sum_{i=1}^{n} \varphi_i^{\Gamma}(X_N; \hat{r}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} F_{ij}^{\Gamma}(r_{N+1})$$

$$+ \sum_{i=1}^{n} \chi_i^{\Gamma}(X_{N+1}) c_{ij}^{\Gamma}$$

- Γ: all conserved quantum numbers in scattering
  L, S, M_L, M_S, π, α (all others that may apply)
- j: a solution label
  E: energy

Atomic multi-channel scattering

$$\psi_{jE}^{\Gamma} = \mathcal{A}\sum_{i=1}^{n} \varphi_i^{\Gamma}(X_N;\hat{r}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} F_{ij}^{\Gamma}(r_{N+1})$$

$$+ \sum_{i=1}^{n} \chi_i^{\Gamma}(X_{N+1}) c_{ij}^{\Gamma}$$

- φ_i: state of scattering target, coupled with ℓ and σ of scattered electron to a total L and total S
- A: antisymmetrisation operator
- F: radial wavefunction for scattered electron

Atomic multi-channel scattering

$$\psi_{jE}^{\Gamma} = \mathscr{A} \sum_{i=1}^{n} \varphi_i^{\Gamma}(X_N; \hat{r}_{N+1}\sigma_{N+1}) r_{N+1}^{-1} F_{ij}^{\Gamma}(r_{N+1})$$

$$+ \sum_{i=1}^{m} \chi_i^{\Gamma}(X_{N+1}) c_{ij}^{\Gamma}$$

- χ_i: “correlation” function involving all electrons to improve near-nucleus wavefunction, where close-coupling description is less accurate
- c_{ij}: expansion coefficients

Closed channels

- Channels without escape are common.
  - Use K-matrix formalism $F = s + cN$
  - n open channels
  - m closed channels $N = \begin{pmatrix} K \\ L \end{pmatrix}$

$$s_{ij}(r) \underset{r\to\infty}{\to} \frac{\delta_{ij}}{\sqrt{k_i}} \sin\vartheta_i, \quad i = 1,...,n+m \quad j = 1,...,n$$

$$c_{ij}(r) \underset{r\to\infty}{\to} \frac{\delta_{ij}}{\sqrt{k_i}} \cos\vartheta_i, \quad i = 1,...,n+m, \quad j = 1,...,n$$

$$c_{ij}(r) \underset{r\to\infty}{\to} \delta_{ij} e^{-\varphi_i}, \quad i = 1,...,n+m, \quad j = n+1,...,n+m$$

$$\vartheta_i = k_i r \ + \text{ corrections}$$

$$\varphi_i = |k_i| r \ + \text{ corrections}$$

Closed channels

- Insertion into

$$F = RF'$$

allows us to transform an (n+m)-by-(n+m) R-matrix into a n-by-n K-matrix and S-matrix.

- Multi-channel R-matrix given by

$$R_{ik} = \sum_j \psi_{ij}(a) \frac{1}{2(E_j - E)} \psi_{kj}(a)$$

where $\psi_{kj}(a)$ is boundary amplitude of inner-region eigenstate j associated with channel k

Orbitals

- Needed:
  - Accurate wavefunction for total system
  - Accurate wavefunction for target
  - No overconvergence of one vs. the other
- Number of functions needed to describe F: around 25 – 75.
- To keep calculations feasible, use small number of functions to describe target states.
- Start by specifying an orbital list used for target-state generation. In Ne, 1s, 2s, 2p, 3s, 3p, 3d

Orbitals

- Target states described using a small CI basis set.
  - Basis set formed by configuration list
  - Example 2-state calculations of Ne^+
    $1s^22s^22p^5$ and $1s^22s2p^6$
  - Configuration list
    $1s^22s^22p^5$, $1s^22s^22p^5$, $1s^22p^6$
    (+ single/double excitations to 3s, 3p and 3d)

- Ground-state orbitals, 1s, 2s, 2p, typically HF orbitals

- Depending on the nature of the calculations,
  3s, 3p and 3d: physical orbitals OR
  pseudo-orbitals to optimise $1s^22s^22p^5$, $1s^22s2p^6$

Correlation functions

- Multi-electron wavefunction has 2 terms
  - Scattering functions
  - Correlation functions

- Correlation functions obtained by adding an extra orbital (from the input orbital list) to an entry in the configuration list

- All allowed combinations are included.

Scattering functions

- Scattering functions: product of a target state plus a continuum function

  Continuum function obtained from diagonalistion of a B-spline basis set in a model potential over the inner region. Bloch operator is included.

- Orthogonality with orbitals
  - Orbitals are projected onto B-spline basis set
  - Diagonalisation proceeds in a manner, which guarantees orthogonality with these orbitals

(Bentley PRA 1993/4)

R-matrix propagation

- Asymptotic expansion may only be sufficiently accurate at a large distance from nucleus
- Multi-electron effects only significant close to nucleus
- Efficient calculation:
  - Determine R-matrix reasonably close to nucleus
  - Propagate R-matrix to the larger distance

R-matrix propagation

- R-matrix propagation requires the Schrödinger equation on an interval with a left and a right boundary (L_L and L_R Bloch operators):

$$\left(H - L_L + L_R - E\right)F = \left(L_R - L_L\right)F$$

- Rewrite in terms of Green's function

$$F = \left(H - L_L + L_R - E\right)^{-1}\left(L_R - L_L\right)F$$

$$= G\frac{1}{2}\left(F_R' - F_L'\right)$$

R-matrix propagation

- Simplify equation by determining the Green's function in Rydberg rather than au.

$$F = G\left(F'_R - F'_L\right)$$

- Now evaluate equation at L and R boundary

$$F_R = G_{RR}F'_R - G_{RL}F'_L$$

$$F_L = G_{LR}F'_R - G_{LL}F'_L$$

- R-matrix equations

$$F_R = RF'_R$$

$$F_L = RF'_L$$

R-matrix propagation

- Now express R_R as function of R_L, G's:

$$F_L = R_L F'_L = G_{LR} F'_R - G_{LL} F'_L$$

$$F'_L = \left(R_L + G_{LL}\right)^{-1} G_{LR} F'_R$$

$$F_R = G_{RR} F'_R - G_{RL} F'_L$$

$$F_R = G_{RR} F'_R - G_{RL} \left(R_L + G_{LL}\right)^{-1} G_{LR} F'_R$$

$$F_R = R_R F'_R$$

$$R_R = G_{RR} - G_{RL} \left(R_L + G_{LL}\right)^{-1} G_{LR}$$

and a propagation scheme for the R-matrix

Time-dependent R-matrix theory

- Start from the non-relativistic time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$

- Approximated in a Crank-Nicolson form as

$$\left(H_{q+1/2} - E\right)\Psi_{q+1} = -\left(H_{q+1/2} + E\right)\Psi_{q}$$

$$E \equiv \frac{2i}{\Delta t}$$

Time-dependent R-matrix theory

- For the inner region, this can be written as

$$\Psi_{q+1} = \frac{1}{\left(H_{q+1/2} + L_b - E\right)}\left(L_b\Psi_{q+1} - \left(H_{q+1/2} + E\right)\Psi_q\right)$$

  which resembles the earlier equations, but with an extra inhomogeneous term

- Additional term leads to slightly more complicated propagation equations

Theory

- Projection onto the outer region channels at the boundary of the inner region gives

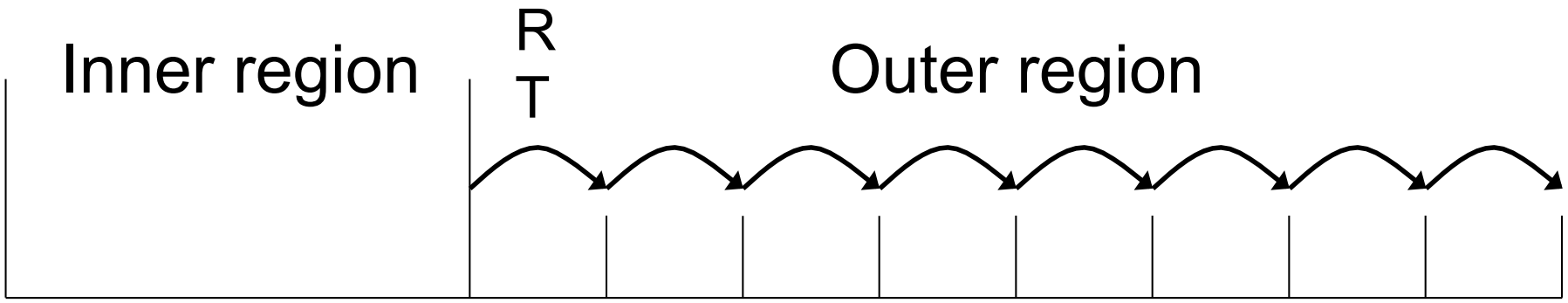
$$F_{q+1}(a) = R \left. \frac{dF_{q+1}}{dr} \right|_{r=a} + T$$

- R: time-dependent equivalent of standard R-matrix, flow of unknown wave function through boundary
- T: vector describing flow from the inner region flow of known wave function
- F: wave function at time-step q+1
  Boundary condition: at large r, F(r) = 0

Time-dependent R-matrix theory

F: known at large r
R,T known at inner region boundary

Divide the outer region into sub-regions
Propagate R and T outward on boundaries



Time-dependent R-matrix theory

R-matrix is propagated outward again using

$$R_R = G_{RR} - G_{RL}\left(G_{LL} + R_L\right)^{-1} G_{LR}$$

T-vector propagation:

$$T_R = J_R + G_{RL}\left(G_{LL} + R_L\right)^{-1}\left(T_L - J_L\right)$$

$$J(r) = -2\int_L^R G(r,r')(H(r') + E)\psi(r')dr'$$

G denotes Green's function on subregion,
R and L indicate right and left boundaries

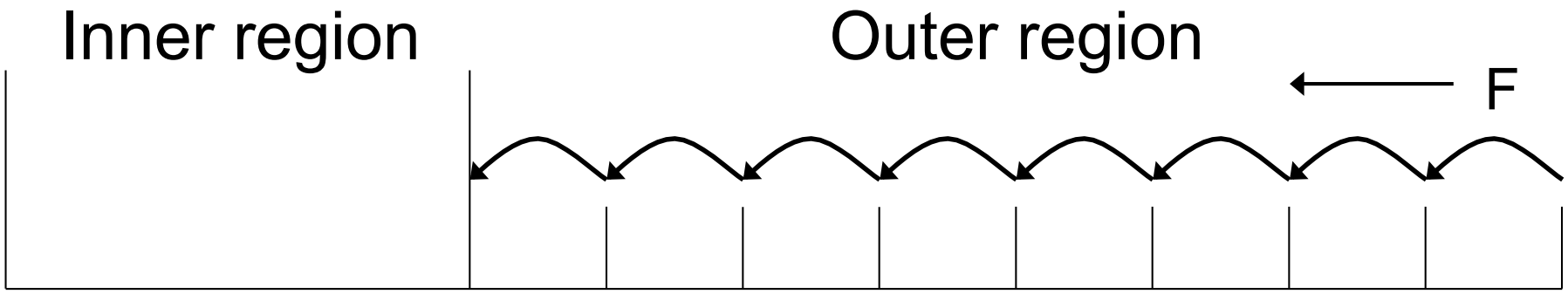
Time-dependent R-matrix theory

F: known at large r

R,T known at all sub-region boundaries

Propagate F inward on sub-region boundaries

F at boundaries → subregion wavefunctions



Time-dependent R-matrix theory

F is propagated inward following

$$F_L = R_L\left(G_{LL} + R_L\right)^{-1} \times$$
$$\times\left[G_{LR}R_R{}^{-1}(F_R - T_R) + G_{LL}R_L{}^{-1}T_L + J_L\right]$$

When F obtained on inner region boundary, use

$$\Psi_{q+1} = \frac{1}{\left(H_{q+1/2} + L_b - E\right)}\left(L_b\Psi_{q+1} - \left(H_{q+1/2} + E\right)\Psi_q\right)$$

to obtain ψ_{q+1} in the inner region

Atomic data

- Atomic data generated by R-matrix II codes using B-spline basis sets
  - Eigenstates for set of L, S, π symmetries
  - Boundary amplitudes / derivatives
  - Dipole matrix elements between eigenstates (Length / V)

- Initial state: inner region: eigenstate
  outer region: 0

- Outer region Green's functions time-consuming
  - Parallelised over outer region sectors
  - Communication: R, T and F
  - Scales well up to ~200 cores

R-matrix theory

- Quick overview of R-matrix theory
- Many subtleties, so much not discussed
  - Buttle correction (avoid if possible: use B-splines)
  - Gauge of field
  - Long-range coupling of asymptotic wavefunctions
  - Double ionization
- Recently developed RMT approach links inner and outer region through another scheme
  - High accuracy in both regions absolutely essential

Conclusions

- General idea about R-matrix theory and its mathematical foundations
- An overview of basic principles
- Show the origin of some of the frequent formulae in R-matrix theory
- Beware of phases, factors of 2 !
- Atomic R-matrix codes written in Fano-Racah phase convention…

Do it yourself

- s-wave scattering off a spherical well
  Phase shift is only possible comparison

- Scattering through a square barrier (1D)
  - 2-channel problem (left, right)
    K-matrix formalism (see closed orbitals):
    s: diagonal 2-by-2 matrix (sin kx)
    c: diagonal 2-by-2 matrix (cos kx)
    Derivatives: s’ diagonal k cos kx
    c’ diagonal –k sin kx

Do it yourself

- Build the R-matrix
- Eigenfunctions within the barrier [-a,a] Boundary conditions $\psi'(-a)=\psi'(a)=0$.
- Diagonalisation of $H+L_R-L_L$ gives (note the constant n=0 solution) :

$$E_n = \frac{1}{2}\left(\frac{n\pi}{2a}\right)^2 + V, \qquad n = 0,\ldots,\infty$$

$$\psi_n(a) = \sqrt{\frac{1}{a}}, \psi_n(-a) = (-1)^n\sqrt{\frac{1}{a}}, \quad n = 1,\ldots,\infty$$

$$\psi_n(a) = \psi_n(-a) = \sqrt{\frac{1}{2a}}, \qquad n = 0$$