Calculations of electron-molecule scattering cross sections using the Rmatrix method

Jimena Gorfinkiel

Department of Physical Sciences
The Open University
Milton Keynes, UK
Jimena.Gorfinkiel@open.ac.uk

July 2014
Outline

- Validity
- What we can calculate
- Basics of the method
- What we can test
- Some ideas on uncertainty determination

'Parameter that characterizes the dispersion of the quantity values that are being attributed to a measurand, based on the information used.'

The meeting is about uncertainties (i.e. precision) and not accuracy although how these are ascertained is related.
The R-matrix method is used (mainly) to determine the electronic part of the scattering problem. Starting from the Born-Oppenheimer approximation it solves the Time-independent Schrödinger equation within the Fixed-nuclei approximation:

\[(H_{N+1}^{(e)} - E)\Psi_{E}^{FN}(\gamma, r; R) = 0\]

\[H_{N+1}^{(e)} = H_{N}^{(e)} - \hat{T}_e(\gamma) + \hat{V}_{int}\]

- The method works best at low energies (below ionization threshold)
- Not normally used for heavy atoms
- Only a few partial waves are calculated (at the moment)
- Integral cross sections, except for elastic scattering
What we calculate

We can calculate:

- electronically elastic cross sections: poorer the higher in energy we go
- electronic excitation cross sections: very dependent on quality of excited states
- resonance parameters: positions better than widths; both shape and core-excited have issues
- near threshold ionization cross sections using pseudostates: poorly
- rotational excitation cross sections
- vibrational excitation of diatomics (of ground and vibrationally excited molecules)

Output from electronic part of the problem (e.g. K-matrices, resonance parameters) are used to feed into other software (e.g. POLYDCS)
R-matrix method

Boundary between regions defined by radius $a$

**Inner region:**
- exchange and correlation important
- multicentre expansion of wavefunction describing scattering electron
- adapt quantum chemistry techniques

**Outer region:**
- exchange and correlation are negligible: long-range multipolar interactions sufficient
Inner region

We want to determine

$$\Psi^E_{FN} = \sum_{k=0}^{\infty} A_k(E) \Psi_k(x_1, x_2 \ldots x_{N+1})$$

Coefficients $A_k$ determined in outer region (or not! needed for photoionisation, bound states, etc.). Energy-independent basis function for specific spatial symmetry expanded as:

$$\Psi_k(x_1, x_2 \ldots x_{N+1}) = A \sum_{ij} c_{ijk} \Phi_i(x_1 \ldots x_N) u_{ij}(x_{N+1})$$

$$+ \sum_i b_{ik} \chi_i(x_1, x_2 \ldots x_{N+1})$$

Associated eigenvalues $E_k$ are known as 'R-matrix poles'.

J.D. Gorfinkel (OU)  e–molecule collisions: R-matrix method  July 2014   6 / 24
Most of the physics are in this expression:

\[ \Psi_k(x_1, x_2 \ldots x_{N+1}) = A \sum_{ij} c_{ijk} \Phi_i(x_1 \ldots x_N) u_{ij}(x_{N+1}) + \sum_i b_{ik} \chi_i(x_1, x_2 \ldots x_{N+1}) \]

- Number and quality of electronic target states \( \Phi_i \)
- Quality of discretized electron continuum given by \( u_{ij} \) and linked to \( a \)
- Quality of short-range corelation polarization linked to \( L^2 \) functions \( \chi_i \)
- \( c_{ijk} \) and \( b_{ik} \) obtained diagonalizing \( (H_{N+1}^{(e)} + L) \). Bloch operator:

\[ L = \frac{1}{2} \sum_{i=1}^{N+1} \delta(r_i - a) \left( \frac{d}{dr_i} - \frac{b}{r_i} \right) \]
Reduced radial functions and surface amplitudes at the boundary:

\[
F_i(a) = \left\langle \frac{(\Phi_j)_i Y_l m_i (\hat{r}_{N+1})}{r_{N+1}} \middle| \psi(E) \right\rangle_{\text{inner}}
\]

\[
f_{ik}(a) = \left\langle \frac{(\Phi_j)_i Y_l m_i (\hat{r}_{N+1})}{r_{N+1}} \middle| \psi_k \right\rangle_{\text{inner}}
\]

\[(\Phi_j)_i Y_l m_i > \text{ Defines a channel. At the R-matrix boundary:}\]

\[
F_i(a) = \sum_{j=1}^{n} R_{ij}(E) \left( a \frac{dF_j}{dr} \bigg|_a - bF_j(a) \right)
\]

R-matrix elements:

\[
R_{ij}(E) = \frac{1}{2a} \sum_k \frac{f_{ik}(a)f_{jk}(a)}{E_k - E}
\]
Total wavefunction can be expanded in the form:

$$\Psi_k(x_1, x_2 \ldots x_{N+1}) = \sum_i \sum_j \Phi_i(x_1 \ldots x_N) \frac{F_j(r_{N+1})}{r_{N+1}} Y_{ljmj}(\hat{x}_{N+1})$$

$F_i(r)$ are solutions of

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{2r^2}\right) F_i(r) + \sum_{j=1}^n V_{ij}(r) F_j(r) = (E - \epsilon_i) F_i(r)$$

We use single centre expansion of

$$V_{ij}(r) = \left\langle (\Phi_s)_i Y_{ljm} \left| \sum_{p=1}^N \frac{1}{r_{p(N+1)}} - \sum_{k=1}^{\text{Nuc}} \frac{Z_k}{\rho_k(N+1)} \right| (\Phi_s)_j Y_{ljm} \right\rangle_{\text{inner}}$$
Coupled differential equations integrated by propagating the R-matrix from the boundary to an asymptotic distance (Light and Walker (1976), Baluja et al. (1982))

Asymptotic expansions used to make the calculation more efficient: Burke and Shey (1962), Gailitis (1976), Coulomb/Bessel

Asymptotically, for a neutral molecule, $F_{ij} \sim 0$ for closed channels and for open ones:

$$F_{ij} \sim \frac{1}{\sqrt{k_i}} \left( (\sin(k_i r - \frac{1}{2} l_i \pi) \delta_{ij} + \cos(k_i r - \frac{1}{2} l_i \pi) K_{ij} \right)$$

Convergence difficult near thresholds. Radii and method of propagation should be tested.
Three basic steps to all calculations:

1. Calculation of target properties: electronic energies ($\epsilon_i$) and transition moments (to generate $V_{ij}$). **Input:** geometry, basis set, molecular orbitals, CI model.

2. Inner region: calculation of $\Psi_k$. **Input:** number of $\Phi_j$, R-matrix radius and continuum basis set, $L^2$ functions.
   - Static exchange (SE): not normally used in production runs
   - Static exchange plus polarisation (SEP): useful for elastic scattering, particularly when studying shape resonances,
   - Close-Coupling: can include large number of target states and pseudostates.

3. Outer region. **Input:** above + propagation details.
In practice:

- $\chi_i$ and $\Phi_i$ (in CC calculations) are generated using a CI model.
- Molecular orbitals expanded in (standard, but some times adapted) basis of GTOs: Hartree-Fock SCF or CASSCF.
- $L^2$ functions $\chi_i$ must be carefully built to ensure $\Phi_i$ and $\Psi_k$ are described to a similar level of accuracy.
- $u_{ij}$ also expanded in a basis of GTOs (currently)
- $a$ determined by spatial-extent of $\Phi_i$ and $\chi_i$

'Model' (basis set, molecular orbitals, CSF/CASSCF active space) chosen to accurately describe: ground state energy and dipole moment and electronic excitation energies. For equilibrium geometry or many. Choice of $\chi_i$ also part of the model.

UKRmol suite freely available from:
http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-in/ and ukrmol-out/
UKRmol suite: target and inner region programs

Diagram illustrating the flow of data and processes involving the software programs SWMOL3, SWORD, SWEDMOS, SWTRMO, CONGEN, SCATCI, GAUSPROP, and DENPROP, highlighting the interactions between pre-processed orbitals, orthogonalized orbital sets, transformed integrals, and target properties.
UKRmol suite: outer region modules
Elastic cross sections: non-dipolar molecule (C$_4$N$_2$H$_6$)

Difference between SE and CC results in this case due to description of polarization. Effect of polarization description linked to model.
Elastic cross sections: polar molecules ($C_4N_2H_6$)

Small angles remain a problem
More examples: pyridine ($C_5NH_5$)

Again, discrepancy in integrated cross sections, even if both are corrected for higher partial waves.
State-to-state inelastic cross section ($\text{H}_2\text{O}$)

(Figure taken from T. N. Rescigno and A. E. Orel, PRA 88 (2013) 012703)
Total inelastic cross section (pyrimidine)

Comparison with experiment

Seemingly 'converged' but not to the experiment.

Effect of changing excitation thresholds
More testing: elastic cross section, HCOOH

- Number of states in close-coupling expansion
- Basis set
- R-matrix radius/continuum description
Some ideas

Within the same method:

- Dependence on target properties: excitation energies, dipole moment, transition moments. Explicit (dipole moment for Born correction) much easier than implicit. Can they be used as indicators of quality of wave functions?

- We already do some of this in R-matrix calculations to select ‘best’ model (we sometimes even publish it)

- If nuclear motion involved: need to assess variation with geometry (and vibrational wavefunctions, etc).

- Run calculations for ‘benchmark’ systems for a number of models: SEP/CC, basis sets, etc.

- how many and how to pick? H₂O, N₂, CH₄,....?

- Which cross sections to look at? Are uncertainties for some cross sections needed more than others?
Comparison between methods can provide a better/different estimate.

- Elastic scattering: integral and differential cross sections determined using a variety of methods (polar molecules more of an issue).
- Pick identical model (say R-matrix and Schwinger: SEP, same geometry, basis, orbitals, N+1 CSF) to estimate 'method uncertainty'
- Electronically inelastic scattering: fewer methods. Experiment may not help much either
- Choose a number of benchmarks at same level of approximation.
- Use knowledge of strength and weaknesses of methods
- Shift in resonance positions can lead to huge change in cross section size: uncertainty in E?
- Consistency: could tell us if determined uncertainties are too small.
The molecular R-matrix method, software and ’know how’ have been developed during at least the last 30 years by a large number of people.

Results presented have been calculated both at the OU and UCL and collaborators.