Perturbative and non-perturbative methods for electron-impact ionization

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Outline

• Background. Electron-impact ionization (EII); why do we care?
• What does perturbative and non-perturbative mean?
• Where does it matter?
• Examples of ionization of small targets – mostly atoms
• Ionization of larger, more complex targets.
• Plasma modeling – why we do all this!

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Electron-impact ionization – what are we trying to do?

• We are trying to predict the cross sections for break-up of atoms and molecules by electron-impact, eg

\[ e^- + \text{He} \rightarrow \text{He}^+ + e_1^- + e_2^- \]

– The ionization probability is represented by a cross section – what can be measured
– Cross sections can come in various forms:
  ▪ Total cross section is just total probability for ionization
  ▪ Differential cross section explores more of the details – cross section as a function of the angle and/or energy of the outgoing electrons

• We can solve directly the Schrodinger equation for such a system since all potentials are known – Coulomb terms in the Hamiltonian can be written down
  – Can’t be solved analytically – “three-body problem”
  – Can be solved numerically – by making various approximations for the wavefunctions of the electrons and for the interaction terms in the Hamiltonian
  – Multi-electron targets require all electron-electron interactions to be considered

\[ H_{\text{atom}} = -\frac{1}{2\nabla_1^2} - \frac{1}{2\nabla_2^2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_1 - r_2|} \]
Theoretical approaches to EII: distorted-wave

A distorted-wave (DW) approach treats the electron-electron interactions perturbatively
- The incident, scattered, and ejected electronic wavefunctions are all ‘distorted’ by the potential of the target atom (including nuclear and electron potential terms)
- One can choose the potential in which the wavefunctions are computed (e.g., ‘post’ or ‘prior’ forms of the interaction potential)
- The interaction between the active electrons (incident and ejected) is often treated to first-order in perturbation theory

Several sets of DW codes are available worldwide, such as LANL codes, FAC, etc.

DW approaches are much less computationally expensive compared to close-coupling approaches

They are accepted to be less accurate for neutral/near-neutral targets, but accuracy appears adequate for moderately and highly-ionized systems

Fully relativistic DW versions are also available, as well as ‘semi-relativistic’ versions (often based on the Cowan code) in which one-electron terms are added into the non-relativistic Hamiltonian
Theoretical approaches to EII: close-coupling

• Close-coupling approaches aim to treat the interaction between the outgoing (scattered & ejected) electrons in a non-perturbative manner in an effort to more accurately model the ionization process
  – Non-perturbative – the interaction between the active electrons is treated to all orders in perturbation theory.

• Several close-coupling approaches have been developed in recent decades:
  – Convergent close-coupling (CCC)
  – R-matrix (with pseudo states) (RMPS) and variants – notably B-spline R-matrix (BSR)
  – Time-dependent close-coupling (TDCC)
  – Exterior complex-scaling (ECS)

• Each of these approaches has advantages/disadvantages
  – Most approaches are quite computationally expensive
  – Fully relativistic versions of many of these approaches are also available
  – Accepted view is that one requires such close-coupled approaches for low-energy, neutral & near-neutral systems for which the electron-electron couplings are strong and cannot be treated perturbatively
Theoretical approaches to EII: advantages/disadvantages

• Perturbative/distorted-wave approaches

  • Advantages
    – Computationally fast
    – Can be straightforwardly combined with atomic structure codes to allow calculations for virtually any atom or ion
    – Convergence is straightforward to assess – usually through partial wave expansions
    – Can be easily extended to calculate ionization from inner shells, not just valence
    – Can be used to understand the physics of the scattering process
  
  • Disadvantages
    – Not accurate for neutral targets and low incident energies
    – Are especially inaccurate when electron-electron interaction is dominant (eg when electrons are emitted with near-equal energies/angles
      ▪ although various “fixes” such as Coulomb repulsion terms, such as Gamow factors, can be added

• Nonperturbative approaches

  • Advantages
    – Should be very accurate – agreement with experiment for simple targets confirms this
    – Can produce all possible scattering processes in one calculation – ie all differential cross sections and all inelastic processes (in principle)

  • Disadvantages
    – Computationally intensive
    – Numerical convergence can be sometimes challenging to confirm
    – Hard to implement for complex (open-shell) targets (eg Fe, W). Most methods restricted to (quasi) one- or two-electron targets, although R-matrix approach is an exception
    – Difficult to treat inner-shell ionization processes
    – “brute-force” calculation – does it allow for physics insight?
Light atoms: total cross sections

• For H, He, & Li close agreement exists between theory & experiment
• Studies on Be also report good agreement between a variety of close-coupling methods
  – Recent study highlighted close agreement between RMPS, CCC, and TDCC methods
  – DW approaches ~ 20-30% higher for neutral atom but quickly approaches close-coupling results by two-times ionized
• Although studies of other light atoms (Z=1-10) are not comprehensive, where comparisons exist, agreement between different close-coupling approaches is generally satisfactory

*Dipti et al, ADNDT 127, 1 (2019)*

*Pindzola & Robicheaux, PRA 61 052707 (2000)*

**FIG. 1.** Total electron-impact ionization cross section for helium. Solid squares: time-dependent close-coupling method, topped up at high angular momentum with distorted-wave results. Solid curve: distorted-wave with exchange method, dashed curve: distorted-wave with no exchange method; solid circles: experimental measurements [11] (1.0 Mb = 1.0 × 10⁻¹⁸ cm²).

**FIG. 1.** Electron-impact ionization cross sections for neutral Be, from (a) the ground 1s²2s² configuration and (b) the first excited 1s²2s2p configuration. The solid lines are the time-dependent close-coupling calculations. The dot-dashed lines are the RMPS calculations and the short-dashed (with crosses) and dotted lines (with squares) are the DWIS(N) and DWIS(N−1) calculations, respectively. The solid line with squares are CCC calculations from Ref. [7]. In (b) all calculations include ionization from both the 2s and 2p subshells. Also, the RMPS calculations are for ionization from the 1s²2s²p ⁴P term only (1.0 Mb = 1.0 × 10⁻¹⁸ cm²).
Angular distributions: state-of-the-art comparison of He ionization

- Measurements at MPI-K in Heidelberg have been able to measure the full angular distribution over most of the solid angle of ejection of the outgoing electron.

- Agreement with non-perturbative methods (here, CCC and TDCC shown) is excellent.

- The measurements and theory are absolute – close-coupling methods produce a fully consistent set of cross sections for all scattering processes in a given calculation.

**TDCS: triple differential cross section – ionization as a function of outgoing electron angle & energy**
Physics insight: Angular distributions from electron-impact ionization of He

- Non perturbative calculations (RMPS as well as CCC and TDCC) were able to explain some features in the angular distributions and trace them to propensities for electron ejection.
Physics insights: Angular distributions and strong minima in TDCS of He

Measurements made in the 1990s showed an unexpected minimum in the angular distributions for electron ionization of helium

Non perturbative & perturbative methods were used to study the physics of the scattering process

A deep minimum was observed in both DW and TDCC calculations

Interference between the partial waves in the quantum-mechanical scattering amplitude is related to the position of this minimum

The minimum is also found for atomic H and molecular H$_2$!
Atomic and molecular signatures for charged-particle ionization

Ola Al-Hagan¹, Christian Kaiser², Don Madison¹* and Andrew James Murray²*

- Experimental studies of scattering from He and H₂ found significant differences for some geometries.
- In a special ‘perpendicular’ geometry, He angular distribution peaked at 180°, but H₂ had a dip there. Why?
- Don Madison’s 3DW calculations (averaged over all molecular orientations), agreed with measurement, unlike plane-wave models. But what is the physics?

- The peak at 180° is caused by an electron scattering from the nucleus after a binary collision with an electron
- Scattering from a point charge (He) results in a different distribution than scattering from two centers (H₂), because the electron-nucleus scattering is stronger when a nucleus is present at the center-of-mass (as in He)
- So the 180° peak is stronger for atomic targets
- This implies scattering from tri-atomic molecules would produce a peak – and it does! CO₂ measurements have a peak at the center
**H₂ scattering analysis – lots of physics to explore**

- A TDCC method for e-H₂ scattering was in development and I was able to compare with Andrew’s measurements. This led to a fruitful collaboration with both Don Madison and Andrew Murray.
- Agreement between TDCC and measurement was good for orientation-averaged cases.
- We were able to use TDCC (and 3DW, later) to examine the angular distributions from oriented H₂ molecules.

**TDCC: time-dependent close-coupling method**
H₂ scattering analysis

Electron-impact-ionization cross sections of H₂ for low outgoing electron energies from 1 to 10 eV

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• Don’s group worked on understanding the importance of PCI to these distributions. This is another example of Don leveraging the tools at his disposal to understand the scattering physics.

• As the impact energy decreases (from 20 to 2 eV), the angular distributions change steadily in shape. Don showed that this was due to the increasing importance of PCI in the lower energy collisions. This is a separate effect from the electron-nucleus scattering found in the He and H₂ comparisons.

• Don also related this to the threshold Wannier theory and was able to interpret his results to explore where this theory applies.

**PCI: Post-collision interaction:**
a measure of the correlation between the outgoing electrons. In the M3DW method, it is represented by a Ward-Macek Coulomb-distortion factor in the final-state wavefunction.
H₂ scattering analysis

There is lots of physics to explore in the physics of electron ionization of molecular H₂ – the molecular alignment at the time of ionization makes a difference to the resulting electron angular distribution patterns.

Non perturbative calculations agree well (but not perfectly) with experiment.
Somewhat heavier atoms; neon

- TDCS measurements from neon were made by the Heidelberg group of Dorn et al.
- They compared very well to two theoretical approaches: the **B-spline R-matrix** (BSR) approach of Bartschat and Zatsarinny, and a **distorted-wave (3DW)** approach of Don Madison and co-workers.
- Comparisons were made for 3 slices through the 3-dimensional plane that the two outgoing electrons can occupy.
- Various incident electron angles and energy sharings between the outgoing electrons were explored.
- Both theories gave very good agreement with the data.

\[ Ne (Z=10) \]
Somewhat heavier atoms; argon

- Measurements were also then made on argon.
- Agreement with the BSR approach was very good; the 3DW comparison was not quite as good.
- Comparisons were again made for slices through the 3-dimensional plane that the two outgoing electrons can occupy.
- As a heavier atom, it can be more difficult to describe the atomic structure correctly; also spin-orbit effects may be important.

Moderately heavy atoms: $Z \approx 11-36$

- For **total** cross sections, fewer close-coupling studies exist – some studies have been published for several noble gas atoms and quasi one-electron (Na) and two-electron (Mg) targets.
- DW approach over-estimates the **absolute** cross section (compared to measurement) for neutral Si (not unexpected)
  - Although we note that at higher energies, the DW approach appears reasonable.

*Colgan et al, PRA 77, 062704 (2008)*

![Graph showing electron-impact ionization cross sections for neutral Si. The partial cross sections from the $3s$ and $3p$ sub-shells of the ground $3s^23p^2$ configuration have been summed to compare with experiment. We compare our present distorted-wave calculations (DW) with the experimental measurements of Freund et al. [11] and binary-encounter-Bethe (BEB) calculations of Stone and Kim [32].]
Moderately heavy atoms: Z~11-36

- DW calculations for $\text{Si}^{2+}$ appear of acceptable accuracy
- And by $\text{Si}^{7+}$ DW appears very accurate
Moderately heavy atoms: Z~11-54

- Transition metals?
  - Not aware of (m)any close-coupling calculations

- Close-coupling approaches generally have difficulty with targets in which the atomic structure is complex
  - TDCC, ECS, and CCC are restricted to (at best) quasi one-electron and two-electron targets
    - And even these calculations may involve approximations with respect to structure
  - R-matrix approach can be applied to complex targets, but convergence can be difficult
  - Relatively few ionization calculations have been performed with R-matrix calculations for heavy atoms – excitation is in some sense easier
  - Preliminary calculations were performed on Mo$^+$ in 2005
    - Correlation and term-dependence in the initial state was explored

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**Mo$^+$**

FIG. 4. Electron-impact single ionization cross section for Mo$^+$ in the 4$^2$S ground configuration. Closed squares connected by solid curve: TDCC calculation for direct ionization, solid curve: TDCC calculation for direct ionization plus TDW calculation for 4p $\rightarrow$ nl excitation-autoionization, open triangles: experimental measurements [6], and open circles: experimental measurements [20].

*Ludlow et al, PRA 72 032729 (2005)*
Electron-impact ionization of $W$: comparison with measurement

- FAC code also used to investigate single ionization of $W^+$ ions
  - Sensitivity noted of the cross section to the choice of local central potential within the FAC calculation
  - Authors used potentials arising from either
    - $W^+$ [5$d^4$6$s + 5$d^5 + 5$d^3_6s^2$ ] or
    - $W^{2+}$ [5$d^3_6s + 5$d^4 + 5$d^2_6s^2$ ]
  - Different cross sections obtained depending on this choice
  - Underlines the difficulty even of the structure calculations that are required for such complex ions
  - Excitation-autoionization is also expected to contribute to the cross section in this case
  - A further complication is that the distorted-wave approximation may also be inaccurate for such low-charged ions

There has been some Dirac R-matrix calculations of electron-impact excitation in recent years by the Belfast/Auburn groups.

Putting this all together – ionization cross sections are needed in plasma modeling

- **Total** ionization cross sections are needed to perform collisional-radiative modeling of partially-ionized plasmas
  - Other inelastic cross sections also required – excitation and inverse processes
  - One requires cross sections from all states of all ions in the plasma – data management can be an issue
  - Examples include atmospheric plasma modeling, and Sn laser-produced plasmas used in lithography

- In radiation-dominated plasmas, **photo-processes** are also needed (photoionization and photoexcitation)
  - A notable example is in the modeling of our Sun, where the photoionization cross sections have recently been questioned
  - In this case (mid-ionized Fe), the perturbative and non-perturbative cross sections are in good agreement

Non-LTE modeling of Sn plasmas is a key component in understanding the plasmas in EUV lithography

LTE modeling of Fe plasmas is key to some of the puzzles remaining in solar modeling
Angular distributions of ionized electrons are also important for modeling magnetically confined plasmas

- **Disruption** in a tokamak plasma:
  - One of the largest uncertainties of the tokamak confinement concept.
  - Disruption event caused by plasma instabilities, etc.
  - Quenches plasma from 5-10 keV to 1-10 eV over a ms. No fusion.
  - Leads to a chain of events that critically damages vessel.
  - We need to safely be able to “turn off” the plasma to mitigate damage.
  - A way to turn “off” the plasma is to inject a mid/high Z element that will act as a coolant, since the higher Z elements radiate power much more efficiently than low Z species.
  - However, these species can & will ionize in the plasma, and the resulting electrons can “runaway” – get accelerated by the plasma fields to extremely high energies. To mitigate this, we need to know where the electrons move and with how much energy. **Atomic physics can help!**

*Our goal is to provide accurate angular distributions from a variety of relevant species to inform plasma kinetic simulations*
Macroscopic codes often neglect microscopic physics

Often, Monte Carlo codes don’t include much atomic physics – in particular, they assume that ionized electrons are ejected isotropically or in the forward direction.

– Is this approximation valid? If not, how much difference would these angular distributions make to the conclusions of the Monte Carlo simulations?

– Hence the need for accurate angular distributions.

\[ e^- (e_{inc}) + Z^{q+}(l) \rightarrow e^- (e_s, \Omega_s) + e^- (e_{ej}, \Omega_{ej}) + Z^{(q+1)+}(u) \]

Our goal is to provide accurate angular distributions from a variety of relevant species to inform plasma kinetic simulations.
Electron-impact ionization collision model for Monte Carlo kinetic simulations

\[ e^-(\varepsilon_{\text{inc}}) + Z^q(l) \rightarrow e^-(\varepsilon_s, \Omega_s) + e^- (\varepsilon_{ej}, \Omega_{ej}) + Z^{(q+1)}(u) \]

Electron energy-sharing:

40- and 100-eV electron-He single differential cross sections. Figure taken from P. Garkot et al. Atoms 10, 60 (2022)

Collision models in MC simulations generally assume:
Equal-energy sharing (\( E_s = E_{ej} \))

Collision models in MC simulations generally assume:
Isotropic scattering, \( l = 1 / 4\pi \)

\[ \frac{d\sigma(\varepsilon_{\text{inc}})}{d\varepsilon_{ej}} = \sigma(\varepsilon_{\text{inc}}) \Sigma(\varepsilon_{\text{inc}}, \varepsilon_{ej}) \int_0^{(\varepsilon_{\text{inc}} - \varepsilon_{\text{ion}})/2} \frac{\Sigma(\varepsilon_{\text{inc}}, \varepsilon_{ej}) d\varepsilon_{ej}}{} = 1 \]

\[ R(\varepsilon_{\text{inc}}, \varepsilon_{ej}) = \int_{\varepsilon_{ej}}^{\varepsilon_{ej}'} \Sigma(\varepsilon_{\text{inc}}, \varepsilon_{ej}') d\varepsilon_{ej}' = \varepsilon_{ej}(R, \varepsilon) \]

\[ \int I(\varepsilon, \Omega) d\Omega = 2\pi \int_0^{\pi} d\theta \sin(\theta) I(\varepsilon, \theta) = 1 \]

\[ R = 2\pi \int_0^{\theta_s} I(\varepsilon_s, \theta_s') d\theta_s' \]

\[ \cos(\theta_s) = \mathcal{F}(\varepsilon_s, R, \ldots) \]

For more details see Ryan Park’s talk on Tuesday: GT2.00005

40.6-eV electron-He triple differential cross section. Figure taken from X. Ren Phys. Rev. A 82, 032712 (2010).
We have developed a new anisotropic angular distribution functions

\[
I(\epsilon, \Omega) = \frac{1}{4\pi} \frac{\epsilon}{[1 + \epsilon \sin^2(\theta/2)] \ln(1 + \epsilon)}
\]

\[
I(\epsilon, \Omega) = C(\epsilon) = \frac{\eta_F(\epsilon)(\eta_F(\epsilon)+1)}{\pi[2\eta_F(\epsilon) + 1 - \cos(\theta)]^2} + \frac{\eta_B(\epsilon)(\eta_B(\epsilon)+1)}{\pi[2\eta_B(\epsilon) + 1 + \cos(\theta)]^2}
\]

For more details see Ryan Park’s talk on Tuesday: GT2.00005

Elastic: e⁻ + He

0-D kinetic simulations of the swarm transport parameters for He. The Park et al. Plasma Sources Sci. Technol. 31, 065013 (2022) model simulations are in excellent agreement with experiment without the need to adjust the data.
71 eV electron-He triple-differential cross sections: New preliminary model

How do our calculations compare to what is used currently in PIC codes?

Squares: TDCC
Dotted-lines: Surendra model:
Solid lines: new model:

\[ I(\varepsilon, \Theta) = \frac{1}{4\pi} \frac{\varepsilon}{[1 + \varepsilon \sin^2(\theta/2)] \ln(1 + \varepsilon)} \]

\[ I(\varepsilon, \Theta) = C(\varepsilon) \frac{\eta_F(\varepsilon)(\eta_F(\varepsilon) + 1)}{\pi [2\eta_F(\varepsilon) + 1 - \cos(\theta)]^2} + [1 - C(\varepsilon)] \frac{\eta_B(\varepsilon)(\eta_B(\varepsilon) + 1)}{\pi [2\eta_B(\varepsilon) + 1 + \cos(\theta)]^2} \]
Conclusions: A suite of methods are available in atomic physics to compute collisional cross sections

**Perturbative** (eg distorted-wave) methods have many advantages; they are
- **Accurate for high electron energies**
- **Accurate for mid and highly ionized ions**
- **Computationally relatively fast to compute**
- It is fairly straightforward to compute ionization from inner-shell states

But..
- They are **not accurate** for low energies and neutral/near-neutral atoms (or molecules)
- This implies DW methods are most suitable for “hot” plasmas where most ions are moderately or highly ionized

**Non-perturbative methods** are useful for neutral/near-neutral systems
- They are **very** accurate when converged because they contain most of the key physics describing the interactions of the incoming and ionized electron.
- However, they have some drawbacks:
  - They are computationally intensive
  - They can be difficult to implement for open-shell systems – R-matrix methods have the best hope
  - Most useful for “low-temperature” plasma modeling

Which method you want to use will depend on what application you care about – ie, what plasma conditions are relevant!

In all cases, atomic & molecular collisional cross sections remains a key quantity in modeling a wide variety of industrial and astrophysical plasmas
Perturbative and non-perturbative methods for electron-impact ionization

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