Time-dependent close-coupling methods for electron-atom/molecule scattering

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Outline of talk

• Theoretical approaches to electron-impact ionization – brief descriptions
  – Time-dependent close-coupling (TDCC) method
    • Strengths and weaknesses
    • Considerations of convergence issues
  – Distorted-wave (DW) approaches
• EII cross sections: overview of calculations performed to date
  – Selected examples of ionization of neutral atoms, ions and a few molecules
• EIE cross sections – less done in this area using TDCC but there are some examples of Li and Be^{q+} ions
• Inclusion of ionization data in public databases
• Conclusions & outstanding issues
  – What still needs to be done
  – A path forward?
TDCC approach to electron-impact ionization

• The TDCC method centers around solution of the time-dependent Schrödinger equation for two interacting electrons

\[ i \frac{\partial P^{LS}(r_1, r_2, t)}{\partial t} = T_{l_1l_2} P^{LS}(r_1, r_2, t) + \sum_{l'_1l'_2} V_{l_1l_2l'_1l'_2} P^{LS}(r_1, r_2, t) \]

• The electron-electron interaction between the outgoing electrons from an ionization process is treated exactly; a close-coupling, or non-perturbative approach

• In electron-impact ionization all possible LS final states are possible (\(1,3S, 1,3P, 1,3D, \ldots\)), and one needs to monitor carefully the convergence with respect to the number of states
  – For moderate projectile energies, the number of partial waves which is required for convergence is usually quite manageable.

• Probabilities for ionization may be extracted at some final time via standard projection methods

• For multi-electron targets, the interaction of the remaining electrons with the two outgoing electrons is treated through additional direct and local exchange potential terms
Why is a time-dependent approach useful?

- The TDCC approach avoids the troublesome boundary condition associated with the three-body Coulomb problem by propagating the equations that describe the electron motion until the interactions are small, and so that converged probabilities for a given scattering process may be extracted.

Plots of the radial component of the total wavefunction show how the two electrons interact.
Uncertainty issues in a TDCC calculation

• Such issues include
  – Radial mesh chosen by user
  – Number of partial waves retained in expansion
  – Whether top-up (with DW partial cross sections) was used and at what partial wave these were applied
  – Choice of core potential for one or two-electron calculations outside of a frozen core

• An experienced user should be able to minimize the uncertainty arising from such considerations, but still tedious and time-consuming testing is the only way to check these issues

• These are “numerical” issues; other more “physics-based” issues also exist
Uncertainty issues in a TDCC calculation

• The interaction of outgoing (active) electrons with the remaining core electrons can lead to uncertainty in the total cross section prediction from TDCC calculations.

• The TDCC approach to ionization is a configuration-averaged approach and so term dependence of the interaction of the outgoing electrons with the core is not properly included.

• Examples of this will be presented for Ne.
**Distorted-wave approach to electron-impact ionization**

- The distorted-wave approach to electron-impact ionization (or excitation) is a well-established method
  - The incident, scattered, and ejected electronic wavefunctions are all ‘distorted’ by the potential of the target atom (including nuclear and electron potential terms)
  - The radial distorted waves are evaluated using a one-electron Hamiltonian of a form similar to

\[
h(r) = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_D(r) + V_X(r),
\]

- These distorted waves are then used to compute Slater integrals which are summed appropriately to calculate the scattering probability
- The incident/scattered/ejected electron radial orbitals each can be computed in either a \( V_N \) or \( V_{N-1} \) potential
  - A common choice is to use the \( V_N \) potential for the incident and scattered orbitals and a \( V_{N-1} \) potential for the ejected orbital
  - Alternatives include computing all orbitals in a \( V_{N-1} \) potential, this leads to better orthogonality properties for the wavefunctions
  - At high energies or for highly ionized targets, either choice produces similar ionization cross sections
- At low energies, or for neutral/near-neutral systems, the two choices can produce different results
- Distorted-wave methods are considered ‘perturbative’ in that the interaction between the electrons is not treated to all orders
Electron-impact ionization of H: Total Cross sections

- Earliest TDCC calculations were made for (e,2e) of H
- Close-coupling calculations (CCC and then TDCC) were shown to provide significantly better agreement with measurement than distorted-wave (DW) calculations
- For H, the DW calculations are ~20-30% larger than the measurements; a trend that persists for many neutral systems
- Progress made since this work - including accurate descriptions of the angular distributions of the outgoing electrons (TDCS) – leads to the acceptance that (e,2e) of H (and H-like systems?) is a solved problem

\[ \text{H}(1s) \]

**FIG. 1.** Total electron-impact ionization cross section for hydrogen. Large crossed boxes, hybrid TDCC plus DW1 method; solid curve, DW1 method; dashed curve, DW2 method; solid circles, experimental measurements [5].

*Pindzola & Robicheaux, PRA 54, 2142 (1996)*
Later calculations dramatically showed how distorted-wave methods become less accurate for more excited states of atoms.

Study was made for H and H-like systems.

This work also clearly shows how the cross section from excited atomic states is much larger than from the ground state.

*Figure 1. Electron-impact ionization cross sections for H(ns) as a function of n. Dot–dashed lines, DW (post form); dashed lines DW (prior form); solid lines, RMPS; crosses, TDCC from Pindzola and Robicheaux [12], open squares, TDCC from Witthoeft et al [2]; solid squares, present TDCC; solid triangles, CCC from Bartschat and Bray [1]; solid circles, experimental measurements of Shah et al [17]; and solid diamonds, measurements of DeFrance et al [18].

Griffin et al, JPB 38, L199 (2005)
Electron-impact ionization of Li$^{2+}$: Total Cross sections

- Also investigated were some H-like ions (Li$^{2+}$);
- DW1 (mixed potentials) does very well for ground state
- Although this is not necessarily true for excited states, where DW approaches appear less accurate

Griffin et al, JPB 38, L199 (2005)
Electron-impact single ionization of He: Total Cross sections

- TDCC calculations for electron-impact ionization of He find similar conclusions to the H ionization work
- Again DW over-estimates measurement for neutral systems by ~20-30%

Pindzola & Robicheaux, PRA 61 052707 (2000)
Electron-impact single ionization of He (1s2s)

- Cautionary tale:
  - Experiment is not guaranteed to be perfect(!)

- For ionization from excited-state He, measured cross sections have been questioned:
  - Three close-coupling calculations are in good agreement with each other but not with measurement
    - Measurement by Dixon, Harrison & Smith made in 1976

- A new measurement here would be most helpful

Electron-impact single ionization of He (1s2s)

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- For ionization from excited-state He, measured cross sections have been questioned:
  - Three close-coupling calculations are in good agreement with each other but not with measurement
    - Measurement by Dixon, Harrison & Smith made in 1976

- PWB calculations in the 70s agreed well with the measurement; seemingly an unfortunate coincidence

*Colgan et al, PRA 66, 062707 (2002)*
Electron-impact single ionization of Li (1s²2s)

Li (1s²2s)

• Electron-impact ionization of Li ground state; again theories agree (TDCC/CCC) but are lower than measurement
  – Measurement made in 1960s
  – Another measurement would be useful also

• For excited state RMPS, TDCC and CCC calculations are all in excellent agreement as well – but no measurements

Colgan et al, PRA 63, 062709 (2001)
A systematic study was performed using TDCC of electron-impact ionization of all Be ions, including excited states.

For neutral Be, 3 methods are in reasonable agreement.

- But no measurements

*Colgan et al, PRA 68, 032712 (2003)*
Electron-impact single ionization of \( \text{Be}^+ (1s^22s) \)

- For \( \text{Be}^+ \) measurements do exist
- Three theoretical approaches agree well with each other but are again lower than measurement
- Perhaps it is time for a campaign to re-measure the ionization from many of these light atomic systems?

*Colgan et al, PRA 68, 032712 (2003)*
Electron-impact single ionization of Be$^{2+}$ (1s$^2$)

- TDCC and RMPS calculations in very good agreement
- DW approaches appear reasonable for this twice-ionized ion
  - But DW less accurate for excited state ionization

*Fig. 5. Electron-impact ionization cross sections for Be$^{2+}$ from (a) the ground 1s$^2$ configuration and (b) the first excited 1s2s configuration. The solid lines are the time-dependent close-coupling calculations. The long-dashed lines (with crosses) are the DWIS(N) calculations and the dotted lines (with squares) are the DWIS(N - 1) calculations. The dot-dashed lines are the RMPS calculations (1.0 Mb = 1.0×10^{-18} cm$^2$).*
Electron-impact single ionization of boron and its ions

• Electron-impact ionization of B \((1s^22s^22p)\)
• TDCC calculations are considerably lower than DW calculations – although no measurements with which to compare
  – DW calculations with mixed potentials exhibit a shape resonance at low energies (unphysical)
  – Binary encounter method due to Y-K Kim in reasonable agreement with TDCC results

\[ \sigma (\text{Mb}) \]

\[ \text{E (eV)} \]

**FIG. 1.** Electron-impact direct ionization cross section for the 2p subshell of the B\((1s^22s^22p)\) ground configuration. Filled squares connected by solid line: TDCC method, dashed line: mixed \(V^N/V^{N-1}\) potential distorted-wave method, dotted line: strictly \(V^{N-1}\) potential distorted-wave method, dot-dashed line: semiempirical binary encounter method [7]. (1 Mb = \(10^{-18}\) cm\(^2\).)

*Berengut et al, PRA 76, 042704 (2007)*
Electron-impact single ionization of B$^+$

- Older measurements made by JILA group of Gordon Dunn
- Measurements did not know fraction of metastable component ($1s^22s2p\,^3P$) in the ion beam
- New measurements at ORNL (Fogle & Bannister) were able to determine a metastable fraction of $\sim 9\%$
- TDCC and RMPS calculations in good agreement with the new measurements
- Further calculations (not shown) appear to confirm the 9% metastable component

**FIG. 1.** (Color online) Electron-impact ionization cross section for B$^+$. Dashed curve: DW method for $1s^22s^2$; connected squares: TDCC method for $1s^22s^2$; solid curve: RMPS method for $1s^22s^2\,^1S$; solid circles: experiment (9% metastable); down triangles: experiment (50% metastable) [5]; and up triangles: experiment (90% metastable) [5] (1.0 Mb=1.0 $\times 10^{-18}$ cm$^2$).

Berengut et al, PRA 78, 012704 (2008)
Electron-impact single ionization of carbon

- Single ionization of neutral C
- TDCC calculations (squares) agree well with measurement
- DW around 15% larger than TDCC calculations at cross section peak
- A more recent TDCC calculation by Abdel-Naby et al, PRA 87, 022708 (2013) also examined excited-state ionization

Electron-impact single ionization of excited carbon ions $C^+ (1s^22s^23s)$

- Single ionization of excited $C^+ (1s^22s^23l)$
- TDCC calculations predict a direct ionization cross section ~ 20% lower than DW calculation
- RMPS calculations significantly higher due to strong excitation-autoionization contribution from terms arising from the $1s^22s2p3s$ configuration

Ballance et al, PRA 84, 062713 (2011)
Electron-impact single ionization of $C^{2+}$

- Joint theory/experimental study of single ionization of $C^{2+}$ ($1s^22s^2$)
- Experiment was able to estimate fraction of ion beam in a metastable state (around 60%)
- RMPS/TDCC/CCC calculations, all made for both ground and metastable states, agree well with measurement using the 40/60% ion beam mixture

Loch et al, PRA 71, 012716 (2005)
Electron-impact single ionization of oxygen ions

- $O^{1+}$ to $O^{4+}$
- Müller group (Giessen, Germany) performed a series of ionization measurements from low-charged $O$ ions
- For $O^+$, TDCC calculations are in good agreement with the measurements

Electron-impact single ionization of neon

Ne \((1s^22s^22p^6)\)

- TDCC calculations are systematically larger than the measurements, as are DW calculations.
- However term-dependent DW calculations (dashed line) lower the computed cross section to close to the experimental result.
  - This term-dependent calculation used the \(2p^5\) kd \(^1\mathbf{P}\) HF potentials in the DW calculation.
  - Instead of the \(2p^6\) configuration-averaged potential.
- Demonstrates that the term-dependence of the outgoing electrons with the \(2p^5\) core needs to be treated accurately.
- It would be desirable to include such Hartree-Fock interactions in a TDCC approach.

Electron-impact single ionization of neon

- Excited-state $2p^53s\ 3P$ term of Ne
- RMPS does well compared to measurement; when averaged over terms, RMPS agrees very well with TDCC

Figure 1. Ionization of the $2p^53s\ 3P$ metastable term of neon. The dashed curve is from the calculation; the dot-dashed curve is from the semiclassical calculation of Deutsch et al [solid curve is from the present RMPS calculation and the solid circles are the experimenta of Johnston et al [11], where the relatively large error bars represent the systematic error smaller ones the statistical error.

Ballance et al, JPB 37, 4779 (2004)
Electron-impact single ionization of neon

- Excited-state $2p^53s \, ^3P$ term of Ne
- RMPS does well compared to measurement; when averaged over terms, RMPS agrees very well with TDCC

Ballance et al, JPB 37, 4779 (2004)
Electron-impact single ionization of silicon

- Ground state of Si
- DW significantly over-estimates measured ionization cross section
- BEB method due to Y-K Kim in reasonable agreement
- No TDCC measurements (yet)

\[
\text{Si} \ (1s^22s^22p^63s^23p^2)
\]

Colgan et al, PRA 77, 062704 (2008)
Electron-impact single ionization of silicon ions

- Ground and excited states of Si\(^{7+}\)
- Highly ionized ion – we compute contributions from 2s & 2p subshells
- DW calculation is in very good agreement with measurement

Colgan et al, PRA 77, 062704 (2008)
Electron-impact ionization of Na & Mg

- Very recent TDCC calculations were made for ionization of Na and Mg
- Calculations made using a newer TDCC version with a better representation of non-ionized core electrons
- To compare against measured angular distributions (TDCS) made by Manchester group
  - Good agreement found in binary & recoil peaks in the TDCS
- Total cross section agreed well with previous measurements

Armstrong et al, PRA 88, 042713 (2013)
Electron-impact double ionization of atoms: \( H^- \)

- 3-electron TDCC calculations were made for double ionization of the \( H^- \) ion
- Not very relevant for modeling, but a good example to demonstrate how theory can discriminate between conflicting measurements
- TDCC calculations in much better agreement with measurements of Defrance group (1992) than with older measurements from Peart & Dolder (1971)
- Other three-electron TDCC calculations have been made for double ionization of He & Be

*Pindzola et al, JPB 39, L127 (2006)*
Electron-impact ionization of molecules: \( \text{H}_2 \)

- First molecular TDCC calculation of electron-impact ionization examined \( \text{H}_2^+ \), then \( \text{H}_2 \)
- TDCC calculation in excellent agreement with measurement
- Angular distributions also available for ionization of \( \text{H}_2 \) by electron-impact
  - These compare quite well with coincidence measurements

*Pindzola et al, PRA 73, 052706 (2006)*
Electron-impact excitation of Li

- TDCC calculation well suited to providing excitation cross sections for one-electron systems
- Comprehensive study of Li excitation cross sections demonstrated good agreement between three close-coupling methods: RMPS/TDCC/CCC
- Convergence in RMPS calculations was also investigated

Griffin et al, PRA 64, 032718 (2001)
Electron-impact excitation of Be$^+$

- RMPS calculations provided comprehensive set of data for all Be ions
- TDCC was used to benchmark the cross sections for Be$^+$
- Agreement again very good between all three methods

Conclusions of quality of TDCC ionization data for modeling

- The Auburn group has demonstrated that use of improved (close-coupling) cross sections for H and He does make a difference to plasma transport studies
  - They also investigated the approximation of using semi-classical approaches or DW approaches instead of close-coupling data
  - This study allowed an assessment of how well such approaches might work for cases where no close-coupling data are available
  - The semi-classical approach was preferred for neutrals but the DW approach was preferred for ions

*Loch et al, PPCF 51, 105006 (2009)*
Ionization data within databases

- All ionization data (from TDCC and other sources) for light elements from H through B have been included in the recent versions of the ADAS database
  - Generalized Rate coefficients as well as raw cross sections are stored
  - Excitation rates also included
  - Published in a series of detailed data papers:
    - Loch et al, PPCF 51, 105006 (2009); “The role of excited state ionization data on H and He generalized collisional radiative coefficients”
    - Loch et al, ADNDT 92, 813 (2006); Generalised collisional-radiative model for light elements. A: data for the Li isonuclear sequence
    - Loch et al, ADNDT 94, 257 (2008); Generalized collisional radiative model for light elements: B: data for the Be isonuclear sequence
    - Loch et al, J Phys Conf Series (2014); Generalized collisional radiative model for light elements: C: data for the B isonuclear sequence
    - Papers forthcoming on the rates for the carbon isonuclear sequence
Conclusions of use of TDCC ionization data for modeling

• We can distinguish between three areas of ionization data for atoms:
  
  – Neutral atoms
  – Excited-states of neutrals & near-neutrals
  – Multiply-charged Ions
Conclusions of use of TDCC ionization data for modeling

• Neutral atoms
  – For one-electron and two-electron systems TDCC performs well and has been shown to give accurate results
  – Compares well to other close-coupling approaches
  – DW approaches, in various forms, typically overestimate cross section by 20-50%, depending on target
  – TDCC is more difficult for atoms in which significant term dependence is exhibited in the initial state
    • i.e. where configuration-average approach is less applicable
Conclusions of use of TDCC ionization data for modeling

• Excited-states of neutrals & near-neutrals
  – TDCC (also other close-coupling calculations) are often more difficult for excited states
    • Due to slower convergence properties with respect to radial mesh, partial wave expansions, etc
  – Calculations performed to completeness should be accurate for one-electron and two-electron systems
  – DW calculations have been shown to become less accurate for excited states of neutrals and few-charged ions
Conclusions of use of TDCC ionization data for modeling

• Multiply-charged Ions
  – DW approaches rapidly become more accurate as the charge on the ion increases
  – Less need for close-coupling approaches when the nuclear charge dominates
  – Broadly speaking, this is true for ions that are more than twice ionized
    • But such assumptions must be checked – especially if excited state ionization is important!
Broader Conclusions for ionization data (1)

• Usually we assume that experiment is the ultimate arbiter to distinguish between calculations and to assess accuracy of data
• However in some cases there is compelling evidence that some measurements need to be looked at again
  – For cases for which two or three close-coupling approaches agree well with each other, but not with measurement
  – Occurs for neutral He*, Li, Be*, and ....
• We encourage more measurements, especially for neutral systems
• These are difficult measurements that must be performed carefully
  – determination of metastable component of ion beam is a challenge
  – also funding constraints are a significant hurdle
• However it is difficult to be truly confident in a data set unless several calculations and several measurements have been performed
  – Is this wish unrealistic today ?!
Broader Conclusions for ionization data (2)

- **Tungsten**
  - We have mostly ignored heavier elements in this talk so far
  - However, W is of prime importance to fusion modeling, and transition metals are often key to understanding astrophysical plasmas
  - DW calculations have been performed for all ions in the W isonuclear sequence
      - Similar calculations also made for the Ar isonuclear sequence
  - The DW calculations are likely to be accurate for moderately and highly-charged ions, but much less accurate for neutral & near-neutral
    - Some evidence that ionization of W$^{4+}$ or W$^{5+}$ ions is reasonably well described
  - However, no close-coupling method has been shown to be feasible for neutral/near-neutral W
  - The significant complexity of the atomic structure of such ion stages is the main reason
  - TDCC methods are unlikely to be applied to such ion stages in the near future
  - RMPS calculations might be possible but are still extremely daunting!
Path forward

• A benchmark study would be a useful way forward for the atomic collision community
  – TDCC methods can contribute to such a study via accurate ionization cross sections, given a suitable system.
  – Unfortunately, ions that might be of most interest to fusion, such as low-charged Tungsten ions, are out of reach from TDCC (and other close-coupling?) calculations at present
  – A lower Z neutral atom or low-charged ion might be most viable candidate for such a benchmark study