OVERVIEW:
I. Production and Assessment of Atomic Data
II. Computational Methods for Electron Collisions
III. Examples for Elastic Scattering, Excitation, Ionization
IV. Conclusions
Electron collisions with atoms, ions, molecules, and surfaces are critically important to the understanding and modeling of low-temperature plasmas (LTPs), and so in the development of technologies based on LTPs. Recent progress in obtaining experimental benchmark data and the development of highly sophisticated computational methods is highlighted. With the cesium-based diode-pumped alkali laser and remote plasma etching of Si$_3$N$_4$ as examples, we demonstrate how accurate and comprehensive datasets for electron collisions enable complex modeling of plasma-using technologies that empower our high-technology–based society.

Electron collisions with atoms, ions, molecules, and surfaces are critically important to the understanding and the modeling of laboratory plasmas, astrophysical processes, lasers, and planetary atmospheres, to name just a few examples. In addition to the investigation of naturally occurring phenomena, electron collisions form the basis of a vast array of plasma-using technologies, which continue to empower our high-technology–based society (1). Atomic, molecular, and optical (AMO) physics, the field that encompasses electron–atom and electron–molecule collisions, has made tremendous contributions to our fundamental understanding of nature. Despite the field’s longevity, breakthrough developments in atomic collisions continue to be made at the fundamental level of both experiment and theory.

The Need for Atomic and Molecular Data

In low-temperature plasmas (LTPs), electron and ion collisions with otherwise unreactive gas and surfaces activate those atoms and molecules through forming excited states, ions, and radicals. Those activated species are then used in applications ranging from microelectronics fabrication (2) to human healthcare (3). The most basic, necessary, and first step in the development of those technologies is the electron or ion impact with the initially unreactive species to produce the activated species. As a result, fundamental AMO physics is closely and beneficially connected to technology development.

Examples of experimental progress in advancing the knowledge base for LTPs include, but are certainly not limited to, the “magnetic angle changer” (MAC) (4) and the so-called “reaction microscope” (RM) (5). The MAC makes it possible to carry out measurements of electron impact cross sections in angular regimes that were previously inaccessible because of geometric limitations due to the position of the electron gun. Furthermore, taking advantage of dramatic improvements in detector technology and fast electronics, the RM has enabled unparalleled detailed studies of electron–atom and electron–molecule collision processes over a wide range of parameters (energies, angles), and so provided an extensive database to test theory.

At the same time, theoretical and particularly computational advances have made the calculation of data for atomic/molecular structure as well as electron collision processes both reliable and cost-effective, and hence enabled their use in models for technology development. Although the basic equations that describe these quantum-mechanical many-body phenomena are believed to be known with a high degree of confidence, their necessarily approximate solution—with an accuracy that allows for reliable quantitative
Production and Assessment of Atomic Data

- Data for electron collisions with atoms and ions are needed for modeling processes in
  - laboratory plasmas, such as discharges in lighting and lasers
  - astrophysical plasmas
  - planetary atmospheres

- The data are obtained through
  - experiments
    - valuable but expensive ($$$) benchmarks (often differential in energy, angle, spin, ...)
    - often problematic when absolute (cross section) normalization is required
  - calculations (Opacity Project, Iron Project, ...)
    - relatively cheap
    - almost any transition of interest is possible
    - often restricted to particular energy ranges:
      - high (→ Born-type methods)
      - low (→ close-coupling-type methods)
    - cross sections may peak at “intermediate energies” (→ ???)
  - good (or bad ?) guesses

- Sometimes the results are (obviously) wrong or (more often) inconsistent!

Basic Question: WHO IS RIGHT? (And WHY???)

For complete data sets, theory is often the "only game in town"!
Topical Review

Uncertainty estimates for theoretical atomic and molecular data

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Abstract
Sources of uncertainty are reviewed for calculated atomic and molecular data that are important for plasma modeling: atomic and molecular structures and cross sections for electron-atom, electron-molecule, and heavy particle collisions. We concentrate on model uncertainties due to approximations to the fundamental many-body quantum mechanical equations and we aim to provide guidelines to estimate uncertainties as a routine part of computations of data for structure and scattering.

Keywords: atomic, molecular, ion, and heavy particle collisions, atomic and molecular structure, electron collisions, uncertainty quantification

(Some figures may appear in colour only in the online journal)

1. Introduction

There is growing acceptance that benchmark atomic and molecular (A+M) calculations should follow accepted experimental practice and include an uncertainty estimate alongside any numerical values presented [1]. Increasingly, A+M computations are also being used as the primary source of data for input into modeling codes. It is our assertion that these data should, if at all possible, be accompanied by estimated uncertainties. However, it is not at all straightforward to assess the uncertainties associated with A+M computations. The aim of this work is to provide guidelines for A+M theorists to acquire uncertainty estimates as a routine part of their work. We concentrate on data that are most important for high-temperature plasma modeling: data for A+M structure, electron-atom (or ion) collisions, electron collisions with small molecules, and charge transfer in ion-atom collisions.

Uncertainty quantification (UQ) is a very active research area in connection with simulations of complex systems arising in weather and climate modeling, simulations of nuclear reactors, radiation hydrodynamics, materials science, and many other applications in science and engineering. A report from the USA National Research Council [2] provides a valuable survey. The current state of the field is reflected in the biennial meeting of the SIAM Activity Group on uncertainty quantification [3]. This field of UQ for complex systems has a mathematical core in the description of uncertainty propagation for chaotic deterministic and stochastic evolution equations in many dimensions (‘polynomial chaos’). In many cases the interest is then focused on systems for which the
Choice of Computational Approaches

- Which one is right for YOU?
  - Perturbative (Born-type) or Non-Perturbative (close-coupling, time-dependent, ...)?
  - Semi-empirical or fully ab initio?
  - How much input from experiment?
  - Do you trust that input?
  - Predictive power? (input ↔ output)

- The answer depends on many aspects, such as:
  - How many transitions do you need? (elastic, momentum transfer, excitation, ionization, ... how much lumping?)
  - How complex is the target (H, He, Ar, W, H₂, H₂O, radical, DNA, ....)?
  - Do the calculation yourself or beg/pay somebody to do it for you?
  - What accuracy can you live with?
  - Are you interested in numbers or “correct” numbers?
  - Which numbers do really matter?
Who is Doing What?
The list is NOT Complete

• “special purpose” elastic/total scattering: Stauffer, McEachran, Garcia, ...
  (some version of Potential Scattering; PS)

• inelastic (excitation and ionization): perturbative
  • Madison, Stauffer, McEachran, Dasgupta, Kim, Dong ...
  (some version of the Distorted-Wave Born Approximation; DWBA)

• inelastic (excitation and ionization): non-perturbative
  • Fursa, Bray, Stelbovics, ... (Convergent Close-Coupling, CCC)
  • Burke, Badnell, Pindzola, Ballance, Gorczyca, ... (“Belfast” R-Matrix, RM)
  • Zatsarinny, Bartschat, ... (B-spline R-Matrix, BSR)
  • Colgan, Pindzola, ... (Time-Dependent Close-Coupling, TDCC)
  • McCurdy, Rescigno, Bartlett, Stelbovics (Exterior Complex Scaling, ECS)

• Molecular Targets: You heard [some of] the main players yesterday.
Classification of Numerical Approaches

- **Special Purpose (elastic/total):** OMP (pot. scatt.); Polarized Orbital

- **Born-type methods:** PWBA, DWBA, FOMBT, PWBA2, DWBA2, ...

  - Fast, easy to implement, flexible target description, test physical assumptions
  - Two states at a time, no channel coupling, problems for low energies and optically forbidden transitions, results depend on the choice of potentials, unitarization

- **(Time-Independent) Close-coupling-type methods:** CCn, CCO, CCC, RMn, IERM, RMPS, DARC, BSR, ...

  - Standard method of treating low-energy scattering; based upon the expansion

    $ \Psi_{LS\pi} (r_1, \ldots, r_N + 1) = \sum_i \int \Phi_{LS\pi} (r_1, \ldots, r_N, \hat{r}) r_F E,i (r) $

    - Simultaneous results for transitions between all states
    - Sophisticated, publicly available codes exist; results are internally consistent

    - Expansion must be cut off (→ → → CC, RMPS, IERM)

    - Usually, a single set of mutually orthogonal one-electron orbitals is used (→ → → BSR with non-orthogonal orbitals)

- **Time-dependent and other direct methods:** TDCC, ECS

  - Solve the Schrödinger equation directly on a grid

  - Very expensive, only possible for (quasi) one- and two-electron systems.
Numerical Methods: OMP for Atoms

• For electron-atom scattering, we solve the partial-wave equation

\[
\left( \frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} - 2V_{\text{mp}}(k, r) \right) u_\ell(k, r) = k^2 u_\ell(k, r).
\]

• The local model potential is taken as

\[
V_{\text{mp}}(k, r) = V_{\text{static}}(r) + V_{\text{exchange}}(k, r) + V_{\text{polarization}}(r) + iV_{\text{absorption}}(k, r)
\]

with

- \( V_{\text{exchange}}(k, r) \) from Riley and Truhlar (J. Chem. Phys. 63 (1975) 2182);
- \( V_{\text{polarization}}(r) \) from Zhang et al. (J. Phys. B 25 (1992) 1893);
- \( V_{\text{absorption}}(k, r) \) from Staszewska et al. (Phys. Rev. A 28 (1983) 2740).

• Due to the imaginary absorption potential, the OMP method

  • yields a complex phase shift \( \delta_\ell = \lambda_\ell + i\mu_\ell \)

  • allows for the calculation of ICS and DCS for
    • elastic scattering
    • inelastic scattering (all states together)
    • the sum (total) of the two processes
Comparison with "ab initio" Close-Coupling

e + I (5p^5, J=3/2)

PRA 83 (2011) 042702

Cross section (a_0^2)

Electron energy (eV)

- BPRM-CC2
- DBSR-CC2
- DBSR-CC2+pol
- DARC-CC11 (Wu & Yuan)
- OMP
Relativistic Effects in Low-energy Electron–Argon Scattering

R. P. McEachran\textsuperscript{A,B} and A. D. Stauffer\textsuperscript{B}

We have performed a relativistic treatment at low energy of electron–argon scattering which includes both polarisation and dynamic distortion effects. Our results are in excellent agreement with the experimentally derived momentum transfer cross section and scattering length, as well as with very recent measurements of the elastic differential cross section.

Extension to account for inelastic effects:

Classification of Numerical Approaches

- **Special Purpose (elastic/total):** OMP (pot. scatt.); Polarized Orbital

- **Born-type methods**
  - PWBA, DWBA, FOMBT, PWBA2, DWBA2, ...
  - fast, easy to implement, flexible target description, test physical assumptions
  - two states at a time, no channel coupling, problems for low energies and optically forbidden transitions, results depend on the choice of potentials, unitarization

- **Time-independent** Close-coupling-type methods
  - CCn, CCO, CCC, RMn, IERM, RMPS, DARC, BSR, ...
  - Standard method of treating low-energy scattering; based upon the expansion
  \[
  \Psi_{L S\pi}(r_1, \ldots, r_N+1) = A \sum_i \int \Phi_{L S\pi_i}(r_1, \ldots, r_N, \hat{r}) \frac{1}{r_F} E_i(r) \]
  - simultaneous results for transitions between all states; sophisticated, publicly available codes exist; results are internally consistent
  - expansion must be cut off (→ → → C CC, RMPS, IERM)
  - usually, a single set of mutually orthogonal one-electron orbitals is used (→ → → B SR with non-orthogonal orbitals)

- **Time-dependent and other direct methods**
  - TDCC, ECS
  - solve the Schrödinger equation directly on a grid
  - very expensive, only possible for (quasi) one- and two-electron systems.
Excitation of Ar $3p^54s$-$3p^54p$ transitions by electron impact

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$^2$Physics Department, Drake University, Des Moines, Iowa 50311

Electron-impact excitation of argon from the $3p^54s$ ($J=0,2$) metastable states to the $3p^54p$ ($J=0,1,2,3$) manifold has been investigated in the semirelativistic first-order distorted-wave and plane-wave Born approximations. The results are compared with recent experimental data of Boffard et al. [Phys. Rev. A 59, 2749 (1999)] and $R$-matrix predictions by Bartschat and Zeman [Phys. Rev. A 59, R2552 (1999)]. In cases for which perturbative approaches are expected to be valid, the plane-wave Born approximation is found to be sufficiently accurate and thus allows for an efficient calculation of results over a wide range of collision energies.

The first-order distorted-wave $T$ matrix for atomic excitation is given by

$$ T_{fi} = (n+1) \langle \chi_f^- (r_0) \Psi_f (\xi) | V - U_f (r_0) | A \Psi_i (\xi') \chi_i^+ (r_0) \rangle. $$

$$ (K + U_f - E_f) \chi_f^- = 0 $$

$$ U_f = \gamma V_f - \frac{1}{4} (\alpha V_f)^2 - \frac{(j+1)}{r} \frac{\eta'}{\eta} + \frac{3}{4} \left( \frac{\eta'}{\eta} \right)^2 - \frac{1}{2} \frac{\eta''}{\eta'}, $$

$$ \gamma = \sqrt{1 + \alpha^2 E_f}, \quad \eta = 1 + \gamma - \frac{1}{2} \alpha^2 V_f $$

polarization and absorption potentials may also be included
Ar $3p^{5}4s \rightarrow 3p^{5}4p$: DWBA vs. R-matrix

**Theoretical results depend on wavefunctions and potentials.**
The target description is ALWAYS an issue.
Electron-impact excitation of argon: Cross sections of interest in plasma modeling

R. K. Gangwar, L. Sharma, R. Srivastava, and A. D. Stauffer

Key Message:
Sometimes BIG Differences between Theories and HUGE Experimental Error Bars!

Which model, if any, can we trust?
Classification of Numerical Approaches

• **Special Purpose (elastic/total):** OMP (pot. scatt.); Polarized Orbital

• **Born-type methods**
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  - two states at a time, no channel coupling, problems for low energies and optically forbidden transitions, results depend on the choice of potentials, unitarization

• **(Time-Independent) Close-coupling-type methods**
  - CCn, CCO, CCC, RMn, IERM, RMPS, DARC, BSR, ...
  - Standard method of treating low-energy scattering; based upon the expansion

\[ \Psi_E^{LS\pi}(r_1, \ldots, r_{N+1}) = \mathcal{A} \sum_i \Phi_i^{LS\pi}(r_1, \ldots, r_N, \hat{r}) \frac{1}{r} F_{E,i}(r) \]

  - simultaneous results for transitions between all states in the expansion; sophisticated, publicly available codes exist; results are internally consistent
  - expansion must be cut off (→ CCC, RMPS, IERM)
  - usually, a single set of mutually orthogonal one-electron orbitals is used for all states in the expansion (→ BSR with non-orthogonal orbitals)

• **Time-dependent and other direct methods**
  - TDCC, ECS
  - solve the Schrödinger equation directly on a grid
  - very expensive, only possible for (quasi) one- and two-electron systems.
Inclusion of Target Continuum (Ionization)

- imaginary absorption potential (OMP)
- final continuum state in DWBA
- directly on the grid and projection to continuum states (TDCC, ECS)
- add square-integrable pseudo-states to the CC expansion (CCC, RMPS, ...)

Inclusion of Relativistic Effects

- **Re-coupling** of non-relativistic results (problematic near threshold)
- Perturbative (Breit-Pauli) approach; matrix elements are calculated between non-relativistic wavefunctions
- **Dirac-based approach**
Time-Independent Close-Coupling

- Standard method of treating low-energy scattering
- Based upon an expansion of the total wavefunction as

\[ \Psi_{E}^{L S \pi}(r_1, \ldots, r_{N+1}) = A \sum_i \Phi_{i}^{L S \pi}(r_1, \ldots, r_N, \hat{r}) \frac{1}{r} F_{E,i}(r) \]

- Target states \( \Phi_i \) diagonalize the \( N \)-electron target Hamiltonian according to

\[ \langle \Phi_i' | H^T | \Phi_i \rangle = E_i \delta_{i'i} \]

- The unknown radial wavefunctions \( F_{E,i} \) are determined from the solution of a system of coupled integro-differential equations given by

\[ \left[ \frac{d^2}{dr^2} - \frac{\ell_i(\ell_i + 1)}{r^2} + k^2 \right] F_{E,i}(r) = 2 \sum_j V_{ij}(r) F_{E,j}(r) + 2 \sum_j W_{ij} F_{E,j}(r) \]

with the direct coupling potentials

\[ V_{ij}(r) = -\frac{Z}{r} \delta_{ij} + \sum_{k=1}^{N} \langle \Phi_i | \frac{1}{r_k - r} | \Phi_j \rangle \]

and the exchange terms

\[ W_{ij} F_{E,j}(r) = \sum_{k=1}^{N} \langle \Phi_i | \frac{1}{|r_k - r|} | (A - 1) \Phi_j F_{E,j} \rangle \]

Close-coupling can yield complete data sets, and the results are internally consistent (unitary theory that conserves total flux)!
In 1998, de Heer recommends 0.5 x (CCC+RMPS) for uncertainty of 10% — independent of experiment!
Metastable Excitation Function in Kr

Experiment: Buckman et al (1983), multiplied by 0.67

51-state Breit-Pauli R-matrix (Bartschat & Grum-Grzhimailo 2000)

Oops — maybe we need to try a bit harder?
Metastable Excitation Function in Kr

Experiment: Buckman et al (1983), multiplied by 0.67

51-state Breit-Pauli R-matrix (Bartschat & Grum-Grzhimailo 2000)
49-state Breit-Pauli B-spline R-matrix

$5s[3/2]_2 + 5s'[1/2]_0$

Cross Section ($a_0^2$)

Electron Energy (eV)

We did! What a difference with BSR :):):)
Key Ideas:
- Use \( B \)-splines as universal basis set to represent the continuum orbitals
- Allow non-orthogonal orbital sets for bound and continuum radial functions

Consequences:
- Much improved target description possible with small CI expansions
- Consistent description of the \( N \)-electron target and \((N+1)\)-electron collision problems
- No "Buttle correction" since \( B \)-spline basis is effectively complete

Complications:
- Setting up the Hamiltonian matrix can be very complicated and lengthy
- Generalized eigenvalue problem needs to be solved
- Matrix size typically \( 100,000 \) or more due to size of \( B \)-spline basis
- Rescue: Excellent numerical properties of \( B \)-splines; use of (SCA)LAPACK \textit{et al.}

Record: 200,000 to do 50-100 times; 0.5 - 1.0 MSU (1 MSU = $50,000 in NSF Accounting)

We also have to solve the problem outside the box for each energy (from 100's to 100,000's).
List of early calculations with the BSR code (rapidly growing)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Authors</th>
<th>Journal</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h\nu + \text{Li}$</td>
<td>Zatsarinny O and Froese Fischer C</td>
<td>J. Phys. B 33 313</td>
<td>2000</td>
</tr>
<tr>
<td>$h\nu + \text{He}$</td>
<td>Zatsarinny O, Gorczyca T W and Froese Fischer C</td>
<td>J. Phys. B. 35 4161</td>
<td>2002</td>
</tr>
<tr>
<td>$h\nu + \text{B}$</td>
<td>Zatsarinny O and Gorczyca T W</td>
<td>Abstracts of XXII ICPEAC</td>
<td>2003</td>
</tr>
<tr>
<td>$h\nu + \text{O}$</td>
<td>Zatsarinny O and Bartschat K</td>
<td>Phys. Rev. A 73 022714</td>
<td>2006</td>
</tr>
<tr>
<td>$h\nu + \text{Ca}$</td>
<td>Zatsarinny O et al.</td>
<td>Phys. Rev. A 74 052708</td>
<td>2006</td>
</tr>
<tr>
<td>$e + \text{He}$</td>
<td>Stepanovic et al.</td>
<td>J. Phys. B 39 1547</td>
<td>2006</td>
</tr>
<tr>
<td>$e + \text{Ne}$</td>
<td>Zatsarinny O and Tayal S S</td>
<td>As. J. S. S. 148 575</td>
<td>2003</td>
</tr>
<tr>
<td>$e + \text{Ar}$</td>
<td>Zatsarinny O and Tayal S S</td>
<td>J. Phys. B 35 2493</td>
<td>2002</td>
</tr>
<tr>
<td>$e + \text{Zn}$</td>
<td>Zatsarinny O and Bartschat K</td>
<td>Phys. Rev. A 71 022716</td>
<td>2005</td>
</tr>
<tr>
<td>$e + \text{Fe}$</td>
<td>Zatsarinny O and Bartschat K</td>
<td>Phys. Rev. A 72 020702(R)</td>
<td>2005</td>
</tr>
<tr>
<td>$e + \text{Kr}$</td>
<td>Zatsarinny O and Bartschat K</td>
<td>J. Phys. B 40 F43</td>
<td>2007</td>
</tr>
<tr>
<td>$e + \text{Xe}$</td>
<td>Allan M, Zatsarinny O and Bartschat K</td>
<td>Phys. Rev. A 030701(R)</td>
<td>2006</td>
</tr>
</tbody>
</table>

at least 80 more since 2006

BIG SURPRISE (discovered through a GEC collaboration): This is not what I learned in "Introduction to Atomic Collision Theory".

Collisions at "intermediate energies": Coupling to the continuum can be very, very important.
Electron-impact excitation of neon at intermediate energies

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(Received 18 July 2012; published 30 August 2012)

Since then, we have shown that this is a general problem in electron collisions with outer p-shell targets (e.g., C, N, F, Cl, Ar).

Convergence and sensitivity studies provide a systematic way to assign some uncertainty to theoretical predictions, which is becoming an increasingly "hot" topic. (PRA editorial 2011, IAEA/ITAMP workshop 2014, ...)

In fact, that's why we are here today.
metastable $4s[3/2]_2$ and $4s'[1/2]_0$ states. Somewhat surprisingly, however, the coupling effect also prevails for the excited states with electronic angular momentum $J = 1$ for incident energies at least up to 100 eV. This fact suggests that simple models, such as a distorted-wave approach, would not be appropriate until such comparatively high energies. Semi-empirical fixes to such models, as suggested by Kim[16] with so-called “BEF-scaling,” may help. However, such methods are limited to particular situations, and success is by no means guaranteed due to the lack of a firm theoretical foundation.

Figure 5. Cross sections for electron-impact excitation of the individual states of the $3p^54s$ manifold in argon from the ground state ($3p^6$)$^1S_0$. The results from a number of BSR calculations with a varying number of states shows the convergence of the CC expansion.

Figure 6. Cross sections for electron-impact excitation of the individual states of the $3p^54s$ manifold in argon from the ground state. The BSR-31 and BSR-500 predictions[48] are compared with a variety of experimental data.[73–76]
metastable $4s[3/2]$ and $4s'[1/2]$ states. Somewhat surprisingly, however, the coupling effect also prevails for the excited states with electronic angular momentum $J=1$ for incident energies at least up to 100 eV. This fact suggests that simple models, such as a distorted-wave approach, would not be appropriate at such comparatively high energies. Semi-empirical fixes to such models, as suggested by Kim\cite{16} with so-called “BEF-scaling,” may help. However, such methods are limited to particular situations, and success is by no means guaranteed due to the lack of a firm theoretical foundation.

Figure 5. Cross sections for electron-impact excitation of the individual states of the $3p^54s$ manifold in argon from the ground state ($3p^6$)$_0$. The results from a number of BSR calculations with a varying number of states shows the convergence of the CC expansion.

Figure 6. Cross sections for electron-impact excitation of the individual states of the $3p^54s$ manifold in argon from the ground state. The BSR-31 and BSR-500 predictions\cite{48} are compared with a variety of experimental data.\cite{73–76}
Calculations for electron-impact excitation and ionization of beryllium

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Abstract

The $B$-spline $R$-matrix and the convergent close-coupling methods are used to study electron collisions with neutral beryllium over an energy range from threshold to 100 eV. Coupling to the target continuum significantly affects the results for transitions from the ground state, but to a lesser extent the strong transitions between excited states. Cross sections are presented for selected transitions between low-lying physical bound states of beryllium, as well as for elastic scattering, momentum transfer, and ionization. The present cross sections for transitions from the ground state from the two methods are in excellent agreement with each other, and also with other available results based on nonperturbative convergent pseudostate and time-dependent close-coupling models. The elastic cross section at low energies is dominated by a prominent shape resonance. The ionization from the $sp^2[P^2(0)]$ and $sp^2[P^2(0)]$ states strongly depends on the respective term. The current predictions represent an extensive set of electron scattering data for neutral beryllium, which should be sufficient for most modeling applications.

Keywords: electron collisions, beryllium, $R$-matrix with pseudostates, convergent close-coupling, $B$-spline $R$-matrix

(Some figures may appear in colour only in the online journal)

1. Introduction

Beryllium is used as a surface material in the JET project [1] and for the plasma-facing walls in ITER [2]. This calls for accurate e-Be scattering data, as evidenced by recent coordinated research projects and technical meetings organized on this topic by the International Atomic Energy Agency [3, 4]. Beryllium is among the most reactive elements, and its high chemical activity as well as its toxicity make it virtually impossible to obtain reliable values of the electron-impact cross sections from direct measurements with traditional setups.

Due to the lack of experimental data, researchers in plasma modeling currently have to rely entirely on theoretical predictions. For this reason, it is important to estimate the accuracy of the available theoretical data. Extensive calculations utilizing state-of-the-art computational methods, such as $R$-matrix with pseudostates (RMPS) [5, 6], convergent close-coupling (CCC) [7], and time-dependent close-coupling (TDCC) [8], were performed already more than a decade ago. All these calculations indicate a slow convergence of the close-coupling expansion for certain transitions and significant effects originating from coupling to the target continuum. Due to the importance of the e-Be collision system, the topic remains under active investigation, with the most recent CCC predictions published in 2015 [9].

The purpose of the present paper is to provide an extensive and complete (for most modeling applications) set of electron scattering data for neutral beryllium, including elastic scattering, momentum transfer, excitation, and ionization from the ground state as well as a number of excited states, including the metastable $(2s2p)^P$ state, which is of particular importance for collisional radiative models. The calculations reported below were carried out with the $B$-spline $R$-matrix...
predictions is very slow. This is important but ultimately not surprising, since the very same effect was seen in e-Mg scattering [26]. As expected, the CCC-409 predictions are in good agreement with those from the BSR-660 model.

The above shape resonance in elastic e-Be scattering has been the subject of numerous calculations with different methods. An overview of the many predictions is given in table III of [28]. The results differ considerably, ranging for positions from 0.1 eV to 1.2 eV and widths from 0.14 eV to 1.78 eV, respectively. In this respect, it is worthwhile to provide the resonance parameters from direct scattering calculations.

The standard determination of such resonance parameters from collision calculations is based on the analysis of the phase shift in the corresponding partial wave. In the vicinity of a resonance, the phase shift $\delta$ behaves as

$$\delta(E) = \delta^0(E) + \tan^{-1} \left( \frac{\Gamma/2}{E - E_r} \right).$$  \hfill (3)

Assuming that the background phase shift $\delta^0(E)$ is a smooth function of energy, the resonance width $\Gamma$ is determined from the inverse of the energy derivative of the phase shift $\delta$ at the resonance energy $E_r$ via

$$\Gamma = 2 \left[ \frac{d\delta}{dE} \right]^{-1}_{E=E_r}.$$  \hfill (4)

Such an analysis for the $P$ partial wave is given in figure 2, and the corresponding resonance parameters are listed in table 3.

We note, however, that this procedure is somewhat ambiguous in the present case. Since the resonance is very wide and located close to the elastic threshold, the energy dependence of the phase shift given in equation (3) is disturbed. As a result, the phase shift increases by less than $\pi$ radians as the energy passes through the resonance.

Table 3. Position ($E$) and width ($\Gamma$) of the shape resonance (in eV).

<table>
<thead>
<tr>
<th>Method</th>
<th>Cross section maximum</th>
<th>Phase analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_r$</td>
<td>$\Gamma$</td>
</tr>
<tr>
<td>BSR</td>
<td>0.354</td>
<td>0.461</td>
</tr>
<tr>
<td>CCC</td>
<td>0.320</td>
<td>0.434</td>
</tr>
</tbody>
</table>

Another possibility, although not unique either, is to define the resonance parameters from the analysis of the relevant partial-wave (here the $P$-wave) cross section. An estimate for the resonance energy is then obtained from the maximum of the cross section while the (full) width is determined from half the height of this maximum. Table 3 also presents the resonance parameters generated in this way. The difference between the BSR and CCC predictions, and the difference between the values obtained in the two ways of analyzing the results, provide an indication of the likely uncertainty of the resonance parameters in the present calculations. Taking the averages of the results obtained in the schemes outlined above, we estimate the position at about 0.31 eV $\pm$ 0.04 eV above the elastic threshold with a
width of 0.40 eV ± 0.06 eV. These parameters differ considerably from the numerous results obtained with model potentials [27] or complex-rotation-based methods [28] methods.

4.2. Excitation

Cross sections as a function of energy for the most important transitions from the \((2s^2)^1S\) ground state and the metastable \((2s2p)^3P^o\) excited state are presented in figures 3–5 for dipole, nondipole, and exchange transitions, respectively. We compare our BSR and CCC predictions with the published RMPS [6] results. For the very weak transitions, we notice some resonance-like structure near and slightly above the ionization threshold. These structures are, indeed, typical for pseudostate calculations, even if the \(N\)-electron and \((N+1)\)-electron configurations are constructed in a fully consistent manner with each other. The degree of visibility depends on the number of points displayed. Note, however, that rate coefficients involve convolution of the cross sections with the appropriate electron energy distribution function. This, together with the small values of the cross sections for which these structures appear, should ensure that there are no serious problems in collisional radiative models that employ our results. Overall, we trust that the very close agreement between several independently obtained results further solidifies the confidence of the plasma modeling community in using these datasets.

4.3. Ionization and grand total cross section

Ionization cross sections are presented in figures 6 and 7. The BSR-660 and CCC-409 ionization cross sections were obtained as the sum of the excitation cross section to all beryllium autoionizing states and the continuum pseudostates. We assumed that the radiative decay of the autoionizing states is negligible in comparison to the autoionization channel. We find very good agreement between the present BSR-660 and CCC-409 results, but the agreement with the earlier RMPS [6] and TDCC results [8] is also very satisfactory for ionization from both the \((2s^2)^1S\) ground state (see figure 6) and the metastable excited \((2s2p)^3P^o\) state (figure 7).

Figure 7 reveals a strong term dependence in ionization of the \((2s2p)^3P^o\) and \(^1P^o\) states. This is essentially due to the well-known term dependence of the 2p orbital [29]. Since the TDCC model employed a 2p orbital that is close to the
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And for non-dipole spin-conserving transitions. Cross sections as a function of collision energy for selected nondipole transitions in beryllium. The present BSR-660 and CCC-409 results are compared with those from an earlier RMPS-280 [6] calculation.

Figure 3. Cross sections as a function of collision energy for selected dipole transitions in beryllium. The present BSR-660 and CCC-409 results are compared with those from an earlier RMPS-280 [6] calculation.

Figure 4. Cross sections as a function of collision energy for selected nondipole transitions in beryllium. The present BSR-660 and CCC-409 results are compared with those from an earlier RMPS-280 [6] calculation.

Figure 5. Cross sections as a function of collision energy for selected exchange transitions in beryllium. The present BSR-660 and CCC-409 results are compared with those from an earlier RMPS-280 [6] calculation.

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Hartree–Fock orbital optimized on the \( \text{sp} \) \( 2s^2 \)\(^2\) state, the TDCC results displayed here are expected to be most appropriate for this state.

Finally, figure 8 exhibits the grand total cross section for electron collisions with beryllium atoms in their \( \text{sp} \) \( 2s^2 \)\(^2\) ground state, i.e., the sum of angle-integrated elastic, excitation, and ionization cross sections. While the elastic cross section provides the largest contribution over the energy range shown, excitation also contributes substantially, approaching 50% for incident energies above 50 eV. Overall, ionization processes represent less than 10% of the grand total cross section. Since the momentum-transfer rather than the elastic cross section is typically important for plasma modeling, it is also shown in figure 8.

5. Summary

We have presented an extensive set of electron scattering data for neutral beryllium, including elastic scattering, momentum transfer, excitation, and ionization processes. While state-to-state excitation cross sections were obtained for all transitions between the lowest 21 states of beryllium, results were presented for only a few selected transitions. The calculations were performed with a parallel version of the BSR code [10], in which a \( B \)-spline basis is employed to represent the continuum functions inside the \( R \)-matrix sphere. Furthermore, we utilize nonorthogonal orbitals, both in constructing the target states and in representing the scattering functions. In order to independently verify the accuracy of the BSR calculations, we also carried out CCC calculations with an entirely different formulation of the problem and the associated computer code. Very good agreement between the BSR and CCC results was found for all calculated cross sections.

The present calculations were motivated to a large extent by the importance of accurate and thoroughly assessed e-Be collision data. For excitation as well as ionization from the ground state and the most important metastable \( \text{sp} \) \( 2s^2 \)\(^2\) state, we essentially confirm, where available, results from earlier RMPS [6] and TDCC [8] calculations. Furthermore, we found a significant term dependence in the ionization results for the \( \text{sp} \) \( 2s^2 \)\(^2\) and \( \text{sp} \) \( 2s2p \)\(^2\) states, respectively.

The elastic cross section at low energies is dominated by a strong shape resonance in the \( L = 1 \), odd-parity channel. Since this resonance is likely of critical importance for transport processes, we carried out a systematic convergence study for its parameters. The present results, namely a position of about 0.31 eV \( \pm \) 0.04 eV above the elastic threshold with a width of 0.40 eV \( \pm \) 0.06 eV, are very different from recent predictions based on a model-potential method [27] and also on a complex-rotation approach [28].
Hartree–Fock orbital optimized on the $2s^2\,{}^1S$ ground state, the TDCC results displayed here are expected to be most appropriate for this state. Finally, figure 8 exhibits the grand total cross section for the excited $1s^22p$ state of $\text{Be}^+$ (obtained with BSR-660).

**Figure 6.** Cross section for electron-impact ionization of beryllium from the $(2s^2)^1S$ ground state. The present BSR-660 and CCC-409 results are compared with those from earlier RMPS-280 [6] and TDCC [8] calculations. Also shown is the partial cross section for producing the excited $1s^22p$ state of $\text{Be}^+$ (obtained with BSR-660).

**Figure 7.** For ionization (and excitation) from excited states. BSR-660 and CCC-409 results are compared with those from earlier RMPS-280 [6] and TDCC [8] calculations.

Hartree–Fock orbital optimized on the $(2s^2)^1P$ state, the TDCC results displayed here are expected to be most appropriate for this state.

Finally, figure 8 exhibits the grand total cross section for electron collisions with beryllium atoms in their $(2s^2)^1S$ ground state, i.e., the sum of angle-integrated elastic, excitation, and ionization cross sections. While the elastic cross section provides the largest contribution over the energy range shown, excitation also contributes substantially, approaching 50% for incident energies above 50 eV. Overall, ionization processes represent less than 10% of the grand total cross section. Since the momentum-transfer rather than the elastic cross section is typically important for plasma modeling, it is also shown in figure 8.

**Figure 8.** BSR-660 and CCC-409 grand total cross section for electron collisions with beryllium atoms in their $(2s^2)^1S$ ground state, along with the contributions from elastic scattering alone as well as elastic scattering plus excitation processes. Also shown is the momentum-transfer cross section.

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Ionization in the Close-Coupling Formalism

• Recall: We are interested in the ionization process

\[ e_0(k_0, \mu_0) + A(L_0, M_0; S_0, M_{S_0}) \rightarrow e_1(k_1, \mu_1) + e_2(k_2, \mu_2) + A^+(L_f, M_f; S_f, M_{S_f}) \]

• We need the ionization amplitude

\[ f(L_0, M_0, S_0; k_0 \rightarrow L_f, M_f, S_f; k_1, k_2) \]

• We employ the \( B \)-spline \( R \)-matrix method of Zatsarinny (CPC 174 (2006) 273) with a large number of pseudo-states:
  • These pseudo-states simulate the effect of the continuum.
  • The scattering amplitudes for excitation of these pseudo-states are used to form the ionization amplitude:

\[ f(L_0, M_0, S_0; k_0 \rightarrow L_f, M_f, S_f; k_1, k_2) = \sum_p \langle \Psi_f^{k_2} | \Phi(L_p S_p) \rangle f(L_0, M_0, S_0; k_0 \rightarrow L_p, M_p, S_p; k_{1p}) \].

This direct projection is the essential idea. It's not based on first principles, but we'll see if it works.
Including correlation in the ground state reduces the theoretical result.

Interpolation yields smoother result, but direct projection is acceptable.

DIRECT PROJECTION is NECESSARY for MULTI-CHANNEL cases!

So far, so good ... Let's go for more detail!

Total cross section = sum of excitation cross sections to positive-energy pseudo-states.
Triple-Differential Cross Section for Direct Ionization experiment: Ren et al. (2011)

A Benchmark Comparison:
(e,2e) on Ar is a very long story. It includes the discovery of an error in the processing of the raw experimental data, which was found by the confidence gained in BSR predictions ...

**The latest: (e,2e) on Ar (3p⁶)**

\[ E_0 = 66 \text{ eV}; \ E_1 = 47 \text{ eV}; \ E_2 = 3 \text{ eV}; \ \theta_1 = 15^\circ \]

X. Ren et al. (Phys. Rev. A 93 (2016) 062704)

The agreement is not perfect, but no other theory (that we know of) gets anywhere near experiment.
Conclusions

• Despite the field’s maturity, **significant innovations are constantly being made to study electron collisions with atoms and molecules** – and they are needed!

• There exist many fruitful collaborations between experimentalists, theorists, and users outside of AMO who need (and use) these data.

• **Experimental benchmark data remain very important to test and push theory!**

• With such benchmark data and comparisons between predictions from highly sophisticated methods in hand, we can finally estimate uncertainties of these predictions.

**Thank You for Your Attention!**