How accurate are theoretical results?

ITAMP

INSTITUTE FOR THEORETICAL ATOMIC MOLECULAR AND OPTICAL PHYSICS

Joint Workshop with IAEA on Uncertainty Assessment for Atomic and Molecular Data

July 7-9, 2014

at ITAMP, Cambridge MA, USA

https://www-amdis.iaea.org/meetings/ITAMP/

Organizers

James Babb
(ITAMP)

Klaus Bartschat
(Drake University)

Bastiaan J. Braams
(IAEA)

H. Chung
(IAEA)

David Schultz
(University of North Texas)

Jonathan Tennyson
(University College Lond

The workshop will bring together experts working on electron collisions with atoms, ions, and molecules, heavy-particle collisions, and electronic structure of atoms and molecules (with structure viewed here as a prerequisite for collision calculations). The primary goals are to come up with reasonable uncertainty estimates for calculations using the various methods of collision physics: perturbative, nonperturbative, time-independent, time-dependent, semi-classical, etc. Generally, the workshop focus will be on theoretical atomic and molecular data relevant to fusion and astrophysical plasmas, where modeling codes mostly use theoretical atomic and molecular data for which assessments of accuracy are necessary. There will also be data users at the meeting, as well as those who manage databases.

I'll start with a few words about e-atom collisions.

[And basically stick to charged-particle collisions.]

Phys. Rev. A **83**, 040001 (2011)

Editorial: Uncertainty Estimates

The purpose of this Editorial is to discuss the importance of including uncertainty estimates in papers involving theoretical calculations of physical quantities.

It is not unusual for manuscripts on theoretical work to be submitted without uncertainty estimates for numerical results. In contrast, papers presenting the results of laboratory measurements would usually not be considered acceptable for publication in *Physical Review A* without a detailed discussion of the uncertainties involved in the measurements. For example, a graphical presentation of data is always accompanied by error bars for the data points. The determination of these error bars is often the most difficult part of the measurement. Without them, it is impossible to tell whether or not bumps and irregularities in the data are real physical effects, or artifacts of the measurement. Even papers reporting the observation of entirely new phenomena need to contain enough information to convince the reader that the effect being reported is real. The standards become much more rigorous for papers claiming high accuracy.

The question is to what extent can the same high standards be applied to papers reporting the results of theoretical calculations. It is all too often the case that the numerical results are presented without uncertainty estimates. Authors sometimes say that it is difficult to arrive at error estimates. Should this be considered an adequate reason for omitting them? In order to answer this question, we need to consider the goals and objectives of the theoretical (or computational) work being done. Theoretical papers can be broadly classified as follows:

1. Development of new theoretical techniques or formalisms.
2. Development of approximation methods, where the comparison with experiment, or other theory, itself provides an assessment of the error in the method of calculation.
3. Explanation of previously unexplained phenomena, where a semiquantitative agreement with experiment is already significant.
4. Proposals for new experimental arrangements or configurations, such as optical lattices.
5. Quantitative comparisons with experiment for the purpose of (a) verifying that all significant physical effects have been taken into account, and/or (b) interpolating or extrapolating known experimental data.
6. Provision of benchmark results intended as reference data or standards of comparison with other less accurate methods.

It is primarily papers in the last two categories that require a careful assessment of the theoretical uncertainties. The uncertainties can arise from two sources: (a) the degree to which the numerical results accurately represent the predictions of an underlying theoretical formalism, for example, convergence with the size of a basis set, or the step size in a numerical integration, and (b) physical effects not included in the calculation from the beginning, such as electron correlation and relativistic corrections. It is of course never possible to state precisely what the error is without in fact doing a larger calculation and obtaining the higher accuracy. However, the same is true for the uncertainties in experimental data. The aim is to estimate the uncertainty, not to state the exact amount of the error or provide a rigorous bound.

There are many cases where it is indeed not practical to give a meaningful error estimate for a theoretical calculation; for example, in scattering processes involving complex systems. The comparison with experiment itself provides a test of our theoretical understanding. However, there is a broad class of papers where estimates of theoretical uncertainties can and should be made. Papers presenting the results of theoretical calculations are expected to include uncertainty estimates for the calculations whenever practicable, and especially under the following circumstances:

1. If the authors claim high accuracy, or improvements on the accuracy of previous work.
2. If the primary motivation for the paper is to make comparisons with present or future high precision experimental measurements.
3. If the primary motivation is to provide interpolations or extrapolations of known experimental measurements.

These guidelines have been used on a case-by-case basis for the past two years. Authors have adapted well to this, resulting in papers of greater interest and significance for our readers.

The Editors

Published 29 April 2011
DOI: 10.1103/PhysRevA.83.040001
PACS number(s): 01.30.Ww

Some Conclusions for Electron–Atom Collisions

- Uncertainty **depends on several factors**, such as the
  - **quantity of interest** (rate coefficient, angle-integrated cross section, angle-differential cross section, ...).
  - **type of transition** (dipole-allowed, dipole-forbidden, exchange only)
  - **collision energy**

Some Conclusions for Electron–Atom Collisions

- Uncertainty **depends on several factors**, such as the
  - **quantity of interest** (rate coefficient, angle-integrated cross section, angle-differential cross section, ...).
  - **type of transition** (dipole-allowed, dipole-forbidden, exchange only)
  - **collision energy**
- Before making statements, therefore, one should **define the cross sections / rates that "most likely" matter**. ("most likely" = covering "xx%" of the cases).

Some Conclusions for Electron–Atom Collisions

- Uncertainty **depends on several factors**, such as the
  - **quantity of interest** (rate coefficient, angle-integrated cross section, angle-differential cross section, ...).
  - **type of transition** (dipole-allowed, dipole-forbidden, exchange only)
  - **collision energy**
- Before making statements, therefore, one should **define the cross sections / rates that "most likely" matter**. ("most likely" = covering "xx%" of the cases).
- K.B.'s **guesses for electron collisions with the valence electrons** of:
  - **H: 3% (CCC, RMPS, TDCC)**
  - **He: 3% (CCC, RMPS – standard or BSR)**
  - **Quasi-one electron systems: light – 10%, heavy – 20%**;
    provided good experimental structure data are used for scaling/adjustment
  - **Quasi-two electron systems: light – 10%**; **heavy – 30%;**
    provided good experimental structure data are used for scaling/adjustment
  - **Noble gases other than He**: **20% (Ne, Ar)**, **30% (Kr), 40% (Xe)**
  - **Open-shell atoms**: **light (30%)**; heavy such as **Fe, W, ... (???)**

More about these methods is in the other talk.

Some Conclusions for Electron–Atom Collisions

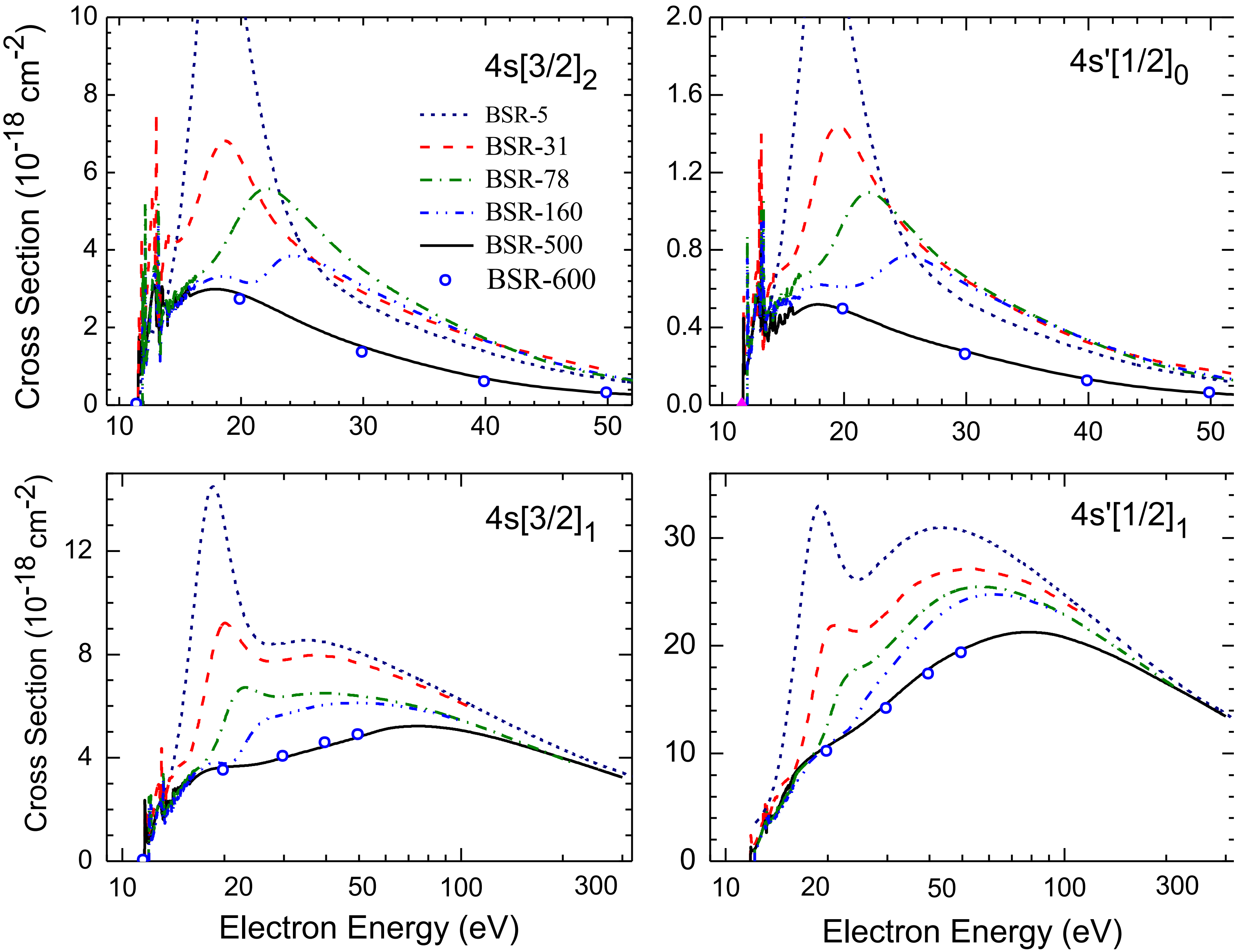
- Uncertainty **depends on several factors**, such as the
  - **quantity of interest** (rate coefficient, angle-integrated cross section, angle-differential cross section, ...).
  - **type of transition** (dipole-allowed, dipole-forbidden, exchange only)
  - **collision energy**
- Before making statements, therefore, one should **define the cross sections / rates that "most likely" matter**. ("most likely" = covering "xx%" of the cases).
- K.B.'s **guesses for electron collisions with the valence electrons** of:
  - **H: 3% (CCC, RMPS, TDCC)**
  - **He: 3% (CCC, RMPS – standard or BSR)**
  - **Quasi-one electron systems: light – 10%, heavy – 20%**;
    provided good experimental structure data are used for scaling/adjustment
  - **Quasi-two electron systems: light – 10%**; **heavy – 30%;**
    provided good experimental structure data are used for scaling/adjustment
  - **Noble gases other than He**: **20% (Ne, Ar)**, **30% (Kr), 40% (Xe)**
  - **Open-shell atoms**: **light (30%)**; heavy such as **Fe, W, ... (???)**
  - **Isoelectronic positive ions** to the above: same or better than neutrals
  - For certain cases (low-energy elastic scattering, optically allowed transitions, ionization), **"special purpose methods"** (polarized orbital, Binary Encounter Bethe, f-scaling) may do very well – maybe even better than "general purpose methods".

Basic Assumptions Behind these Estimates

- Purely numerical errors (mesh, partial-wave convergence, ...) should be negligible for "expert users".
- **Structure problems are real**, but **can be accounted for** to some extent (adjust energy levels, scale oscillator strengths, ensure correct polarizabilities, ...)
- **Relativistic effects** either do not matter enough or are accounted for sufficiently.
- **Convergence checks are performed to the extent possible.**

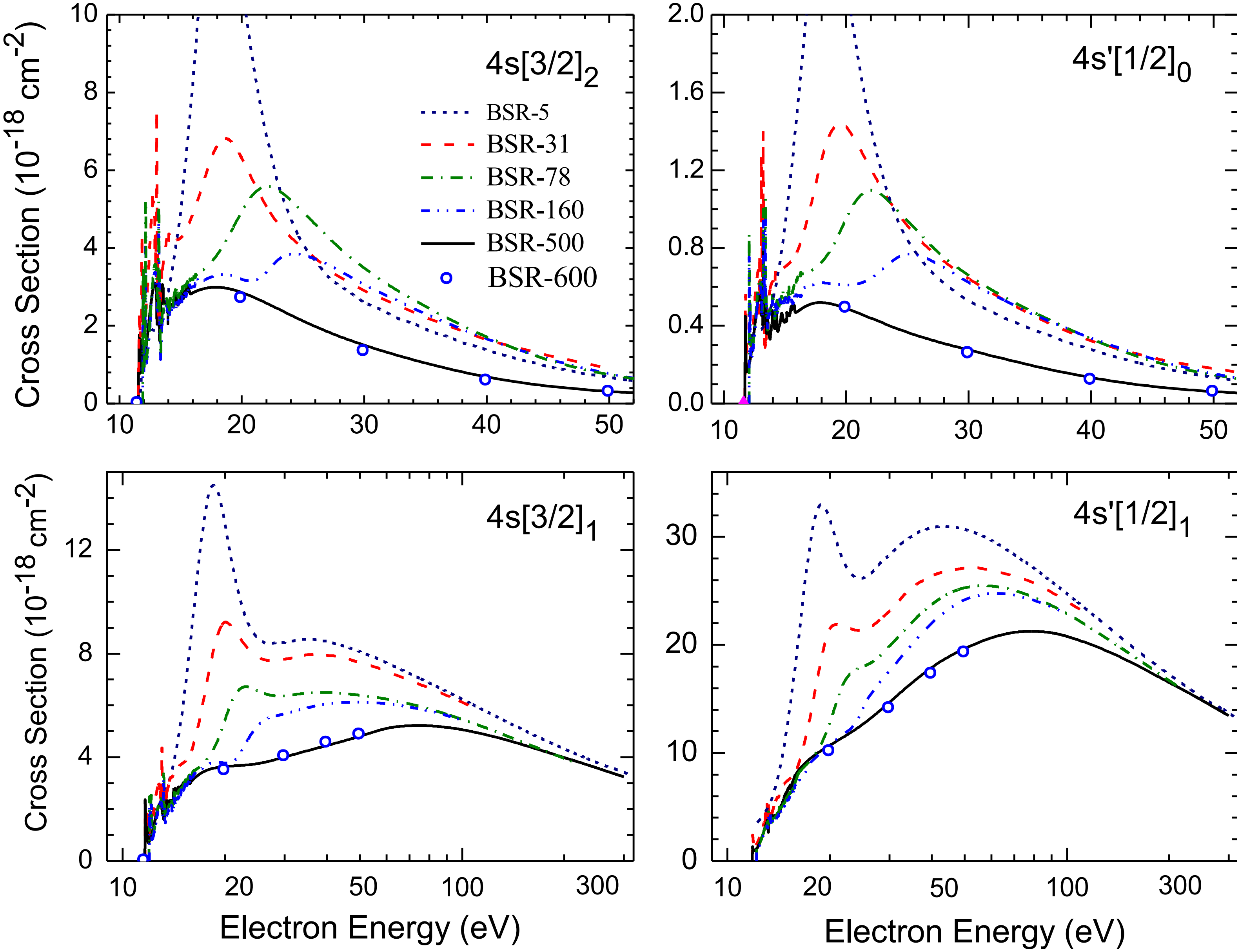
Total Cross Section for Electron Impact Excitation of Argon

Convergence of the Results with Number of Coupled States



Total Cross Section for Electron Impact Excitation of Argon

Convergence of the Results with Number of Coupled States



BSR-600 is the best we can do right now.
The results seem to have converged, but there is guarantee – just hope.

Basic Assumptions Behind these Estimates

- Purely numerical errors (mesh, partial-wave convergence, ...) should be negligible for "expert users".
- **Structure problems are real**, but **can be accounted for** to some extent (adjust energy levels, scale oscillator strengths, ensure correct polarizabilities, ...)
- **Relativistic effects** either do not matter enough or are accounted for sufficiently.
- **Convergence checks are performed to the extent possible.**
- **Some comparison with experiment.**
- **Comparison of available from CCC, RMPS, BSRMPS, TDCC, ...**
- **No "bad surprises"** (no variational principle for $N-$electron and $(N+1)-$electron systems combined)

UCL

e$^-$

Uncertainty Estimation in Electron-Molecule Collisions

Jonathan Tennyson

University College London

Inner region

Outer region

ITAMP
July 2014

This was Jonathan's job (some edits by K.B. for appearance only).

Processes at low impact energies

Elastic scattering

$AB + e \longrightarrow AB + e$

Rotational excitation

$AB(N'') + e \longrightarrow AB(N') + e$

Vibrational excitation

$AB(v''=0) + e \longrightarrow AB(v') + e$

Dissociative recombination/Dissociative attachment

$AB + e \longrightarrow A + B$

Electronic excitation

$AB + e \longrightarrow AB^* + e$

Impact dissociation

$AB + e \longrightarrow A + B + e$

Impact ionisation (e,2e)

$AB + e \longrightarrow AB^+ + e + e$

Why perform electron-molecule collision calculations?

1. To model and interpret experiment
Necessary to demonstrate validity and limitations of theoretical procedure

2. To provide data on unmeasured processes
Eg BASECOL, Phys4Entry
Essential to provide some estimate of uncertainties

Sources of Uncertainty

1. Target model
2. The code/theoretical formalism
3. Scattering model

Target Model

1. Dipoles if non-zero (and other target moments)

Rotational excitation,
elastic scattering,
electronic excitation

Cross section is proportional to μ^2

So uncertainty approx $2\ \Delta\mu / \mu$

TABLE VIII. Dipole moment of water at equilibrium

.

Contribution	Value (a.u.)	Uncertainty (a.u.)
Nonrelativistic, all electron	0.7310	0.0005
Relativistic correction	−0.0017	0.0001
Vibrational averaging	0.0001	0.0001
Final value for the ground-state dipole	0.7294	0.0006
Experimental value (Clough et al, 1973)	0.7296	0.0002

L. Lodi, R.N. Tolchenov, J. Tennyson, A.~E. Lynas-Gray, S.V. Shirin, N.F. Zobov, O.L. Polyansky, A.G. Csaszar, J. van Stralen & L. Visscher,
J. Chem. Phys., 128, 044304 (2008)

Also

L. Lodi, J. Tennyson and O.L. Polyansky,
J. Chem. Phys., 135, 034113 (2011)

Target Model (continued)

2. (Electronic) Excitation energies:
often available from experiment or better theory

3. Target wavefunctions

Codes, Formalism, Numerical Approximations, R-matrix, Schwinger, Kohn, etc.

- Code comparisons: generally satisfactory
- Numerical approximations (grids, basis set truncation, etc.):

  generally well-understood and not major

Scattering Models

- **mmmm...**
  Usually major source of (unquantified) uncertainty

- **Solution?**
  Repeat with variety of models?
  Systematic study e.g. using pseudo-state methodology?
  Benchmark problems: e.g. N_2 and dipolar system?

Heavy-Particle Collisions

David Schultz (Univ. of North Texas)

(summarized by Klaus Bartschat, Drake University)

Conclusions

- **The need for both refined (i.e., with better accuracy as determined via uncertainty quantification assessing both the level of model solved and the numerical convergence of the solution) and new heavy-particle collision data for fusion (and other applications) persists, frequently requiring not only improved and quantified uncertainty, but also completeness (e.g., in the range of energies, states, or scattering angles spanned).**

Conclusions

- **The need for both refined (i.e., with better accuracy as determined via uncertainty quantification assessing both the level of model solved and the numerical convergence of the solution) and new heavy-particle collision data for fusion (and other applications) persists, frequently requiring not only improved and quantified uncertainty, but also completeness (e.g., in the range of energies, states, or scattering angles spanned).**

- **Owing to the evolution of principal interests of the field of atomic, molecular, and optical physics and declining support for atomic data centers and data production in certain countries, the historical approach based on human-resource-intensive compilation of bibliographies, collection of heavy-particle collision data sets, and evaluation via inter-comparison of data sets, cannot be sustained, nor do the most recent needs for comprehensive data sets fit with this model.**

- **The way forward is to update existing data sets for heavy-particle collisions and produce new ones using demonstrably convergent methods that solve as directly as possible the underlying dynamical equations, validated when possible by the remaining (but also diminishing in number) atomic, molecular, and optical experimental activities, or by less direct comparison with plasma experiments.**

Caveats

- At present, **even though certain fundamental heavy-particle collision data sets exist** (or could be produced) **that are demonstrably more accurate numerically** and which are based on treatments with less significant approximations to the dynamical equations solved, **modelers and experimentalists may still adopt more conveniently available** (or "entrenched") data.

Caveats

- At present, **even though certain fundamental heavy-particle collision data sets exist** (or could be produced) **that are demonstrably more accurate numerically** and which are based on treatments with less significant approximations to the dynamical equations solved, **modelers and experimentalists may still adopt more conveniently available** (or "entrenched") data.

- For example, they may judge that **the effort to make such a switch**, possibly necessitating the repeating of extremely long series of simulations or experimental analyses, and their uncertainty about changing data sets without proof that their results would be affected significantly, **provides a barrier to adopting the improved data.**

Caveats

- At present, **even though certain fundamental heavy-particle collision data sets exist** (or could be produced) **that are demonstrably more accurate numerically** and which are based on treatments with less significant approximations to the dynamical equations solved, **modelers and experimentalists may still adopt more conveniently available** (or "entrenched") data.

- For example, they may judge that **the effort to make such a switch**, possibly necessitating the repeating of extremely long series of simulations or experimental analyses, and their uncertainty about changing data sets without proof that their results would be affected significantly, **provides a barrier to adopting the improved data.**

- In addition, even recognizing the very great theoretical and computational progress made to date, **the size and scope of some heavy-particle collisions**, particularly those involving very high n-levels (e.g., as in charge exchange recombination spectroscopy of highly charged ions such as those of tungsten) or many-centers and electrons (e.g., particle-surface interactions) **will therefore require careful validation in comparison with direct atomic-scale experiments or with plasma experiments.**

Caveats

- At present, **even though certain fundamental heavy-particle collision data sets exist** (or could be produced) **that are demonstrably more accurate numerically** and which are based on treatments with less significant approximations to the dynamical equations solved, **modelers and experimentalists may still adopt more conveniently available** (or "entrenched") data.

- For example, they may judge that **the effort to make such a switch**, possibly necessitating the repeating of extremely long series of simulations or experimental analyses, and their uncertainty about changing data sets without proof that their results would be affected significantly, **provides a barrier to adopting the improved data.**

- In addition, even recognizing the very great theoretical and computational progress made to date, **the size and scope of some heavy-particle collisions**, particularly those involving very high n-levels (e.g., as in charge exchange recombination spectroscopy of highly charged ions such as those of tungsten) or many-centers and electrons (e.g., particle-surface interactions) **will therefore require careful validation in comparison with direct atomic-scale experiments or with plasma experiments.**

Thank You!