Uncertainty quantification of theoretical atomic and molecular collisional data

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Fusion requires a huge set of AM data

Mostly Theoretical Data Available

EFDA Task Force
EUROPEAN FUSION DEVELOPMENT AGREEMENT
INTEGRATED TOKAMAK MODELLING

AM processes for kinetic modelling of H

Volume Processees	Reaction Formulas	Ref.
1) e-induced atomic elastic	$e + H \leftrightarrow e + H$	[16]
2) e-induced atomic ionization	$e + H \rightarrow 2e + H^+$	[16]
3) e-induced vibrational excitation eV	$e + H_2(\nu) \leftrightarrow e + H_2(w)$	[16]
4) e-induced vibrational excitation EV	$e + H_2(\nu) \rightarrow e + H_2(w) + h\nu$	[16]
5) molecular ionization	$e + H_2(\nu) \rightarrow 2e + H_2^+$	[16]
6) dissociation	$e + H_2(\nu) \rightarrow e + 2H$	[16]
7) dissociative ionization	$e + H_2(\nu) \rightarrow 2e + H + H^+$	[16]
8) molecular electronic excitation	$e + H_2(\nu) \rightarrow e + H_2^*$	[16]
9) dissociative attachment	$e + H_2(\nu) \rightarrow H + H^-$	[16]
10) molecular assisted recombination MAR	$e + H_2^+ \rightarrow 2H$	[17]
11) mlecular assisted dissociation MAD	$e + H_2^+ \rightarrow e + H^+ + H$	[17]
12) molecular assisted ionization MAI	$e + H_2^+ \rightarrow 2e + 2H^+$	[17]
13) p-induced atomic elastic	$H^+ + H \leftrightarrow H^+ + H$	[18]
14) p-induced elastic/vibrational excitation	$H^+ + H_2(\nu) \leftrightarrow H^+ + H_2(w)$	[18]
15) ion conversion	$H^+ + H_2(\nu) \rightarrow H_2^+ + H$	[18]
16) p-induced dissociation	$H^+ + H_2(\nu) \rightarrow H^+ + 2H$	[18]
17) charge exchange with atom	$H_2^+ + H \rightarrow H^+ + H_2(\nu)$	[19]
18) charge exchange with molecule	$H_2^+ + H_2(\nu) \rightarrow H_2(w) + H_2^+$	[17]
19) collision induced dissociation	$H_2^+ + H_2(\nu) \rightarrow H^+ + H + H_2(\nu)$	[17]
20) electron detachment	$H^- + e \rightarrow 2e + H$	[17]
21) charge exchange recombination	$H^- + H^+ \rightarrow 2H$	[17]
22) electron detachment with atom	$H^- + H \rightarrow H_2(\nu) + e$	[17]
23) electron detachment with molecule	$H^- + H_2(\nu) \rightarrow H + H_2(\nu) + e$	[17]

[16] R. Celiberto, *et al.*, Atomic Data and Nuclear Data Tables **77**, 161 (2001).
[17] R.K. Janev, W.D. Longer, K. Evants, Jr., D.E. Post, *Elementary Processes in Hydrogen-Helium Plasmas* (Berlin: Springer, 1987).
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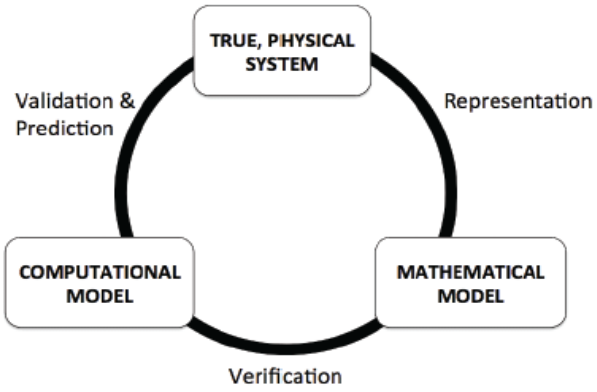
"Plasma-Neutral Interaction in Kinetic Models for the Divertor Region"
F. Taccogna, R. Schneider, K. Matyash, S. Longo, M. Capitelli, and D. Tskhakaya
Contrib. Plasma Phys. 48, No. 1-3, 147 – 152 (2008) / DOI 10.1002/ctpp.200810026

Critical Assessment for Modeling of Physical Processes (VVUQ)



- Verification. The process of determining how accurately a computer program ("code") correctly solves equations of the mathematical model.
- Validation. The process of determining the degree to which a model is an accurate representation of the real world from the perspective of the intended uses of the model
- Uncertainty quantification (UQ). The process of quantifying uncertainties associated with model calculations of true, physical QOIs

- For Optimization-based designs of complex systems and components (e.g. divertor), a comprehensive modeling is required and its VVUQ are critical.
- Majority of available data sets required as input parameters for a modeling are theoretical or computational, most of which are not provided with uncertainty.
- UQ, data evaluation and internationally agreed recommended data library for fusion relevant AM/PSI data are long-term objectives of the Unit.

Uncertainties associated with AM data

- UQ less developed for AM data compared to nuclear data

  AM data look for the solution of an appropriate many-body quantum system with known (Coulombic) interaction compared to nuclear data field reliant on models calibrated to experimental data

- Uncertainty in fundamental parameters outside the domain of atomic and molecular physics

  Fine structure constant, electron-to-proton mass ratio, and in nuclear properties, the mass, magnetic dipole moment, electrostatic quadrupole moment and finer details of the charge distribution of nuclei involved in the system under consideration

- Uncertainty in the fundamental equations, before the introduction of a tractable model

  Various approximations at the level of the basic equations (relativistic contributions, Born-Oppenheimer approximation etc)

Uncertainties associated with AM data(2)

- Uncertainty in the model for many-body quantum mechanics

  Non-relativistc many-body Schrödinger equation is intractractable at a fundamental level (Reduced descriptions: HF, DFC, CCC, etc)

- Uncertainty due to discretization of the model equations

  A finite basis of atomic orbitals for atomic and molecular systems or a Fourier-space discretization in the case of electronic structure calculations for condensed phase (Truncation error)

- Uncertainties beyond the quantum mechanical treatments

  Reduction to classical calculations; for example trajectory calculations using Newton's equations for motion of nuclei (molecular dynamics) with use of an interaction potential

  The representation of the potential is now an important source of uncertainty that is difficult to quantify.

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A starting point

- May 13 — TM (CCN) on General Guidelines for Uncertainty Assessments of Theoretical Data
- Jul 14 — Joint IAEA-ITAMP TM on Uncertainty Assessment for Theoretical Atomic Molecular Scattering Data
- Jun 15 — CM on Guidelines for Uncertainty Quantification of Theoretical Atomic and Molecular Data

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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.

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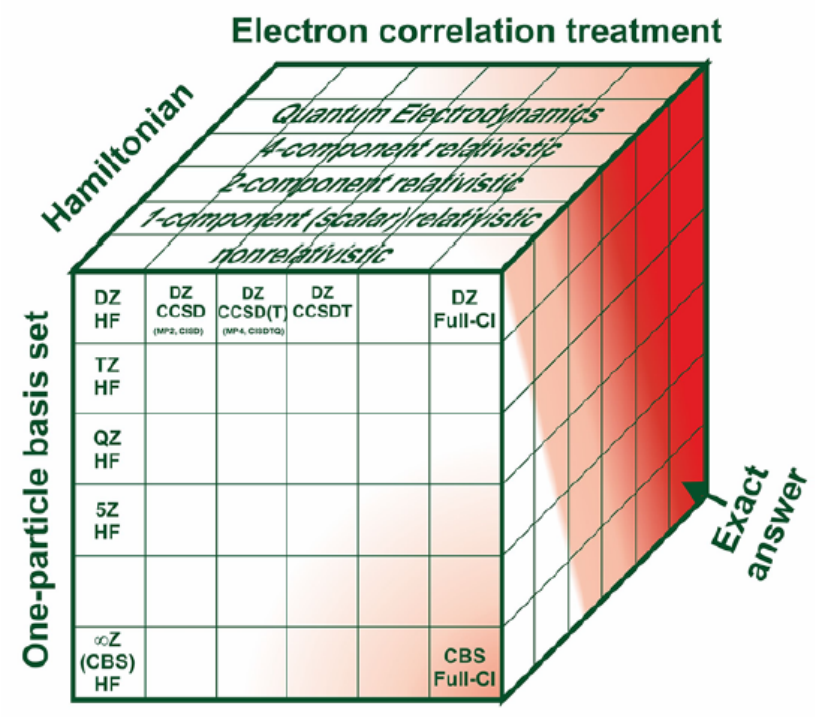
Atomic and Molecular Structure

- Hydrogen exactly solved for nonrelativistic wave function and energy; uncertainties due to relativistic, QED corrections, finite nuclear size etc
- Non-hydrogen; Electronical Hamiltonian, particle basis sets, electron correlation treatment, Born-Oppenheimer approximation(Molecule)

Focal Point Analysis (FPA)



1. Use a family of basis sets (aug-cc-pVXZ etc) which are systematically changed to the completeness,
2. Apply lower levels of theory (typically, HF etc) with very extensive basis sets,
3. Execute high order correlation treatments
4. Examine the added correlation increments.

Ab initio contributions to the first Dissociation energy of $H_2{}^{16}O$.

		Value	UQ
A	CBS CCSD(T) frozen core	43 956	6
B	Core correlation CCSD(T)	+81	2
C	All-electron CBS CCSD(T)[=A+B]	44 037	6
D	Higher order electron correlation	-52	3
E	CBS FCI [=C+D]	43 985	7
F	Scalar relativistic correction	-53	3
G	QED (Lamb shift) correction	+3	1
H	Spin–orbit effect	−69.4	1
I	Angular momenta coupling, OH	+31.5	0
J	Sum spin effects, OH [=H+I]	-37.9	1
K	DBOC, H_2O	+35.3	0.5
L	ZPE H_2O	4638.1	0
M	ZPE OH	1850.7	0.5
N	Net ZPE, H_2O [=L+M]	2787.4	0.5
U	Nonadiabatic contribution	0	1
V	Total MD, H_2O [=I+K+N+U]	-2721	1
	$D_o(H_2O)$ Calc. [=E+V]	41 145	8
	(Obs—Calc) $D0(H_2O)$	+1	-

Uncertainties are given in the last column

All values are in cm^{-1}

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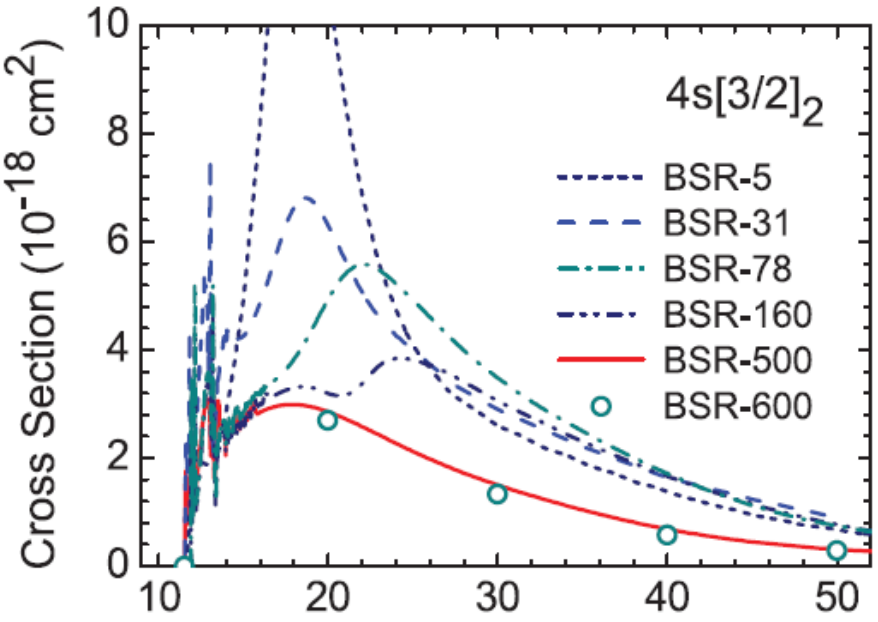
Collisional AM data

- Uncertainty estimates for scattering data are even less developed than structure data as they should include uncertainties of structures as well as reaction probabilities.
- Scattering dynamics change as a function of collision energy and hence one should apply different methods to calculate data of different energy ranges
- UQ: Choice of Hamiltonian (relativity, QED etc), electron correlation, basis sets and the treatment of exchange effects between the projectile electron and target electrons
- For Molecules: need to consider nuclear motion as well as electron motion (vibrational, rotation, dissociation processes)

UQ of AM Collisional Data

Angle-integrated cross-sections for electron impact excitation of the $3p^5 4s$ in argon from the ground state$(3p^6)\ ^1S_0$

Convergence with basis sets



Cross sections for *n*-shell selective charge transfer in C^{6+} -H(1*s*) collisions as functions of impact energy

Discrepancies due to different approximations