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Uncertainty Assessment for Theoretical Atomic and Molecular Scattering Data

Summary Report of a Joint IAEA-ITAMP Technical Meeting

Institute of Theoretical Atomic, Molecular and Optical Physics, Cambridge, MA, USA

7-9 July 2014

Prepared by

Hyun-Kyung Chung, Klaus Bartschat, Jonathan Tennyson and David R. Schultz

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IAEA Nuclear Data Section
Vienna International Centre, P.O. Box 100, 1400 Vienna, Austria

Nuclear Data Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna
Austria

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Abstract

This report summarizes the proceedings of the Joint IAEA-ITAMP Technical Meeting on "Uncertainty Assessment for Theoretical Atomic and Molecular Scattering Data" on 7-9 July 2014. Twenty-five participants from ten Member States and one from the IAEA attended the three-day meeting held at the Harvard-Smithsonian Center for Astrophysics in Cambridge, Massachusetts, USA and hosted by the Institute of Theoretical Atomic, Molecular and Optical Physics (ITAMP). The report includes discussions on the issues of uncertainty estimates for theoretical atomic and molecular scattering data. The abstracts of presentations presented in the meeting are attached in the Appendix.

October 2014

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1. Introduction

A Technical Meeting (TM) on “Uncertainty Assessment for Theoretical Atomic and Molecular Scattering Data” was held at the Harvard-Smithsonian Center for Astrophysics in Cambridge, MA, USA during 7-9 July 2014. The meeting was organized jointly with the Institute of Theoretical Atomic, Molecular and Optical Physics (ITAMP) and attended by twenty-five participants from ten Member States and one from the IAEA. The goal of this meeting was to bring together a number of experts working on electron collisions with atoms, ions, and molecules, heavy-particle collisions, and electronic structure of atoms and molecules in order to come up with reasonable uncertainty estimates for calculations using various methods of collision physics.

Since 2012, the IAEA Atomic and Molecular Data Unit (A&M Unit) has organized five meetings on the topic of data evaluation. At the TM on “Data Evaluation for Atomic, Molecular and Plasma-Material Interaction Processes in Fusion” in Daejeon, September 2012, it was concluded that the lack of uncertainty information of calculated data is one of the biggest technical challenges. In addressing the uncertainty in “physical” measurements, the Reference Guide to the expression of Uncertainty in Measurement (GUM) was published by the Bureau International des Poids et Measures (BIPM) and adopted by numerous international organizations (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML). However, hardly any guide or work exists to critically evaluate calculated atomic and molecular collisional data.

More recently, an interest in the uncertainty estimates of computational model results has steadily grown in the community of engineering and physical sciences. The National Research Council (NRC) of the US National Academies has recognized the importance and need of critical assessment for modeling of physics processes and issued a report on “Assessing the Reliability of Complex Models: Mathematical and Statistical Foundations of Verification, Validation, and Uncertainty Quantification” (Washington, DC: The National Academies Press, 2012). While computational models are ubiquitous to study physical processes and design engineering work, their representation of reality is not perfect due to flaws and uncertainties. The inherent limitations with models should be addressed to give a level of confidence to those who use the results of computational models. The report lists three types of limitations associated with models: 1) ***Verification (V):*** The process of determining how accurately a computer program (“code”) correctly solves the equations of the mathematical model. 2) ***Validation (V):*** 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. 3) ***Uncertainty quantification (UQ):*** The process of quantifying uncertainties associated with model calculations of true, physical quantity of interest (QOI), with the goal of accounting for all sources of uncertainty and quantifying the contributions of specific sources to the overall uncertainty.

The work on uncertainty estimates of theoretical and evaluated data sets is already on the way for nuclear data, for example in the recent paper by M. E. Rising, et al. "Uncertainty quantification of prompt fission neutron spectra using the Unified Monte Carlo method," (Nuclear Data Sheets, 118, 360-363, (2014)). The Bayesian theorem and the Monte-Carlo method are combined to assign overall uncertainties to calculated nuclear scattering data.

The aim of the present meeting was to provide inputs for a technical document that outlines the guidelines for critically assessing theoretical atomic and molecular data, and motivate theoretical physicists in the atomic and molecular collisions community to investigate the uncertainties of their theoretical method. The work on the guidelines has already begun at the TM of the 3rd Code Centre Network in 2013, where strategies to develop guidelines for uncertainty estimates of calculated atomic and molecular structure and collision data were discussed. Guidelines need to take into account target, resolution or observable of interest (or QOI) and specific theoretical methods employed in calculations. In order to motivate theoretical physicists in the broader community, the Unit collaborated with ITAMP, a leading organization in theoretical atomic and molecular physics, to host the meeting. ITAMP hosts concentrated workshops and topical group meetings, trains postdoctoral fellows and receives visiting scientists and speakers in the field. It was possible to invite the most pronounced experts in the community, many from the USA, to the meeting only due to the financial and organizational help from ITAMP.

In this meeting, participants presented technical details of various methods employed in calculating atomic and molecular collisional data and the possible uncertainty components in their methods. The list of participants can be found in Appendix 1 and the meeting agenda in Appendix 2. Summaries by participants are in Appendix 3. Participants discussed ways to estimate uncertainties of theoretical data in technical sessions led by Profs Klaus Bartschat, Jonathan Tennyson, and David Schultz. This report outlines the proceedings of the meeting, presentations and discussions on the issues of the uncertainty estimates of theoretical atomic and molecular scattering data.

2. Proceedings of the Meeting

Dr H. Sadeghpour, the director of ITAMP, welcomed participants and acknowledged the importance of uncertainty estimates of theoretical atomic and molecular data. The opening address was followed by the presentation on the background and objectives of this meeting by the scientific secretary, Dr H. Chung of the IAEA, and by a presentation on the recent change in the policy of the journal of Physical Review A (PRA) by the Editor in Chief, Prof G. Drake. Presentations were given on various methods and their uncertainties for electron-atom, electron-molecule and heavy particle scattering data as well as atomic and molecular structure data. On the last day, Dr D. Reiter provided an overview of atomic and molecular data needs for fusion applications followed by the presentations of Dr Yu. Ralchenko on the need of data and data quality information for collisional modeling, and Dr A. Kramida on the Monte-Carlo methods to assess uncertainties of theoretical atomic transition probabilities. Slides of the presentations are available on the Unit web page http://www-amdis.iaea.org/meetings/ITAMP/.. Presentations are briefly described here and detailed summaries are presented in Appendix 3.

2.1 Overview Presentations

UNCERTAINTY ESTIMATES: A NEW EDITORIAL STANDARD

Prof Drake of University of Windsor, Canada, reviewed the background and rationale, the statement and implementation of the new policy by the journal of Physical Review A that authors should perform a critical evaluation of their work. Uncertainty estimates would be required whenever practicable, and in particular in 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. The new policy has now been in effect and about 100 papers have been affected since 2010. As a result, papers are more interesting and have greater impact, and the culture of the field is changing so that the inclusion of uncertainty estimates is becoming the new norm, at least in some areas (e.g., structure and spectroscopy).

STATUS OF A&M DATABASE AND DATA ANALYSIS FOR FUSION EDGE PLASMA TRANSPORT STUDIES

Dr Reiter of Forschungszentrum Jülich GmbH, Germany, reviewed the needs of atomic and molecular (AM) data for fusion edge plasma transport. AM data are of significant relevance in fusion boundary layer plasmas, because reactive processes actively influence (and even control) the plasma flow and divertor dynamics in the near target surface domain in reactors. These data are an important ingredient in fusion transport simulations such as in predicting the ITER divertor detachment or machine operation lifetime and impurity plasma cooling. Data at the most detailed level enter such transport simulations in kinetic (microscopic) model components, i.e. neutrals (atoms and molecules, molecular ions, and weakly ionized impurity ions), whereas the macroscopic (fluid) components use condensed, reduced information and atomic collision processes. The unprocessed raw AM data is available through the database HYDKIN (www.hydkin.de) of the EIRENE Monte Carlo code and error propagation and sensitivity analysis are provided as well.

ASSESSING UNCERTAINTIES OF THEORETICAL ATOMIC TRANSITION PROBABILITIES WITH MONTE CARLO RANDOM TRIALS

Dr Kramida of National Institute of Standards and Technology, USA, described strategies for estimating uncertainties of theoretical calculations, particularly applicable for calculated transition probabilities: 1) Investigate internal uncertainties of the model by varying its parameters and comparing results. 2) Investigate internal uncertainties of the method by extending the model and looking at convergence trends. 3) In some cases, a general estimate of internal uncertainties can be obtained by comparing results calculated in different gauges. 4) Investigate possible contributions of neglected effects. 5) Investigate external uncertainties of the method by comparing with results of other methods. He demonstrated the step 1) by implementing a Monte Carlo method with Cowan's suite of atomic codes. A control code was written to randomly vary the input parameters with a normal statistical distribution around initial values with a certain standard deviation. The Slater parameters used in the calculations were adjusted to fit experimental energy levels with Cowan's least-squares fitting program. The standard deviations of the fitted parameters were used as inputs of the control code to provide the distribution widths of random trials for these parameters. Errors propagate through the matrix diagonalization and summation of basis state expansions and lead to significant variations in the resulting transition rates. These variations vastly differ in their magnitude for different transitions, depending on their sensitivity to errors in parameters. With this method, the rate uncertainty can be individually assessed for each calculated transition.

UNCERTAINTIES OF MOLECULAR STRUCTURAL PARAMETERS

Prof Császár of Eotvos University, Hungary, described methods to obtain molecular structure parameters and associated uncertainties. The most fundamental property of a molecule is its structure, the knowledge of which is a prerequisite to determine other properties of molecules. While there are experimental, empirical, and theoretical techniques to determine structures of molecules, different techniques correspond to different structure definitions and thus yield different structural parameters. In the 4th age of quantum chemistry, one can bridge quantitatively the gap between 'effective', experimental and 'equilibrium', computed structures at even elevated temperatures of interest thus minimizing any real uncertainties of structural parameters. It is possible to obtain first-principles predictions of structural parameters of any kind with reliable uncertainty estimates but this procedure is constrained at the moment to molecules containing no more than about 4 atoms. It is possible to obtain very accurate molecular structures by experimental means when the number of molecular parameters is not large but the standard deviation of the fit is definitely not a good indicator of the accuracy obtained. With the joint clever use of experiment and theory one can routinely achieve the 0.001Å and 0.1° accuracy which previously could characterize only the most elaborate experiments.

DATA QUALITY AND NEEDS FOR COLLISIONAL-RADIATIVE MODELING

Dr Ralchenko of National Institute of Standards and Technology, USA, reviewed on data needs for collisional-radiative (CR) models. CR calculations typically require large sets of atomic data and the completeness and consistency of data sets take priority over quality although the latter can never be ignored. Moreover, high-accuracy collisional parameters, such as cross sections, are needed to set up benchmarks for CR datasets. Since CR models are generally problem-tailored, some parameters may be of no importance for one task but crucial for another. New problems in plasma spectroscopy requiring a new kind of datasets that have never been important before were described. Monte Carlo simulations were presented as a powerful and universal technique to study error propagation in CR models.

2.2 Methods in Heavy Particle Collisions

HEAVY-PARTICLE COLLISIONS INVOLVING MANY ACTIVE ELECTRONS: HOW (IN-) ACCURATE ARE OUR CALCULATED CROSS SECTIONS?

Prof Kirchner of York University, Canada, presented an example of uncertainty assessment of heavy-particle collision data. For many-electron multi-center systems, it is too complex to solve explicitly the time-dependent Schrödinger equation (TDSE) of the collision system and one solves (at most) a model, though sophisticated, to describe the collision system. Therefore one has to deal with a two-fold problem when it comes to estimating the uncertainties and inaccuracies of the calculated data: (i) to assess the limitations of the model, (ii) to perform careful convergence studies for the numerical procedures involved. In many cases, a comparison with experimental data is the guideline and it would be difficult to assess their accuracy if experimental data for comparison is not available. Given the complexity of these collision systems it is still a long way to performing calculations with predictive power and known uncertainties. It is suggested to test models on many systems as possible, apply different variations for sensitivity analysis and do this in a systematic and open way.

SENSITIVITY, ERROR AND UNCERTAINTY QUANTIFICATION: INTERFACING MODELS AT DIFFERENT SCALES

Prof Krstic of Stony Brook University, USA, emphasized that evaluations and subsequent choice and recommendation of the atomic and molecular data for use in modeling of plasma applications are critically dependent on the data validation, verification and uncertainty analysis and quantification. The choice of the theoretical method, accuracy and time needed for calculation of the desired data is strongly conditioned by the sensitivity of the plasma model to the data uncertainty. Key terminologies to define uncertainties of atomic, molecular and optical (AMO) data were described and a few examples of AMO data uncertainties, aleatoric and epistemic uncertainties in the heavy particle collision data and atomistic modeling of plasma–material interaction (PMI) process were presented. Aleatoric uncertainties refer to the inherent randomness of phenomenon of interest and epistemic uncertainties are often caused by a lack of understanding or by incorrect knowledge on the phenomenon, characterized by use of insufficient number of parameters, or by the wrong or inaccurate parameters. In order to decrease the epistemic uncertainties, mutual validation of theory/simulation and experiment is highly important.

UNCERTAINTIES OF ELECTRON CAPTURE CROSS SECTIONS IN Be^{4+} + H(1s) COLLISIONS.

Prof Méndez of Universidad Autonoma de Madrid, Spain, presented the investigation on the uncertainties of charge cross-sections in ion-atom-collisions by using four computational methods of semi-classical treatment: Molecular Orbital Close Coupling (MOCC), Atomic Orbital Close Coupling (AOCC), the Classical Trajectory Monte Carlo method (CTMC) and Lattice Time-Dependent Schrödinger equation (LTDSE) method. Considered are n-partial charge exchange (CX) cross-sections in one-electron systems, Be^{4+} + H(1s) collisions. For one-electron systems, theoretical methods are well established and the uncertainties can be estimated by means of a convergence study of the calculation. However, it is not easy to extend these ideas to many-electron systems, where high-energy calculations are often based on the application of the independent electron approximation. At low collision energies, the quality of the basis functions is critical in the description of many-electron collisions.

2.3 Methods in Electron-Atom Collisions

THE PROPAGATION OF CORRELATED UNCERTAINTIES FROM THEORETICAL COLLISIONAL CALCULATIONS THROUGH TO PLASMA SPECTRAL DIAGNOSTICS

Dr Ballance of Auburn University, USA, demonstrated how electron-atom collisional cross-sections interact to provide uncertainty in a magnetic fusion / astrophysical plasma diagnostic. With the increase of computational power over the last two decades, first-order collisional processes such as electron-impact excitation, di-electronic recombination and electron-impact ionization can be calculated in sufficiently reasonable time, that the question of uncertainty for each process can be addressed in a systematic manner. Two methods referred to as ‘baseline’ and ‘method sensitivity’ were suggested for the generation of such uncertainties on the aforementioned collisional rate coefficients. From either method the uncertainties can be carried through collisional-radiative models to produce uncertainties on excited populations, photon emissivities and impurity transport coefficients. 'Method sensitivity' is more rigorous, where a particular collisional theory such as the R-matrix, can be employed in a Monte Carlo approach to determine the sensitivity of the final results to the likely spread of initial conditions. More work needs to be done and the funding and computer support at national supercomputer facilities are critical.

TIME-DEPENDENT CLOSE-COUPLING METHODS FOR ELECTRON-ATOM/ MOLECULE SCATTERING

Dr Colgan of Los Alamos National Laboratory, USA, presented a theoretical description of the time-dependent close-coupling (TDCC) method and described the sources of uncertainties and the ways to estimate the uncertainties. The TDCC method gives an accurate representation of the interaction between two outgoing electrons moving in the presence of a Coulomb field by solving the time-dependent Schrödinger equation for two interacting electrons. In this method, one treats the electron-electron interaction essentially in an exact manner (within numerical accuracy) and a time-dependent approach avoids the difficult boundary condition encountered when two free electrons move in a Coulomb field (the classic three-body Coulomb problem). The most important parameters determining the accuracy of the calculation are the extent and grid spacing of the radial mesh, the number of partial waves retained in the expansion, and the time for which the wavefunctions are propagated. A reasonable way to estimate uncertainties is to make detailed comparisons with other theoretical approaches, especially methods that, in principle, treat the electron-electron interaction rigorously via close-coupling expansions. Such comparisons made for electron-impact ionization cross sections from light atoms show variations in the ionization cross sections of (usually) less than 20%, which can be thought of as a first step in estimating the uncertainty of these cross sections. For heavier systems, the uncertainty is likely to be larger, since the more complex atomic structure and more involved interactions between the core and outgoing electrons makes close-coupling calculations significantly more difficult.

AN EVALUATION OF THE ACCURACY OF THE RELATIVISTIC DISTORTED-WAVE APPROXIMATION FOR THE CALCULATION OF CROSS SECTIONS FOR THE EXCITATION OF ATOMS BY ELECTRON IMPACT

Prof Stauffer of York University, Canada reviewed the sources of uncertainties in the Relativistic Distorted-Wave Approximation (RDW) for electron-atom scattering. It uses the standard formula for the T matrix with solutions of the Dirac equations for both the target wave functions as well as the scattered wave. The method is valid for higher energies and does not give reliable cross sections near threshold and does not include any resonance behavior. The major source of uncertainty beyond the limitations of the method is the quality of the target wave functions themselves. Though these wave functions can be obtained to arbitrary accuracy by including more states in the configuration-interaction description of the target, in practice, we are limited to a finite set of the most important configurations describing the target states. The differential cross-sections (DCS) for scattering in the forward direction are proportional to the oscillator strength for the transition and hence it must be accurate to ensure a correct magnitude of the integrated cross sections. Other indicators of the accuracy of the target wave functions include the agreement between the length and velocity forms of the oscillator strengths, the energies of the various fine-structure levels and the correct energy ordering of these levels.

UNCERTAINTIES IN B-SPLINE R-MATRIX CALCULATIONS FOR ELECTRON-ATOM AND ELECTRON-ION COLLISIONS

Dr Zatsarinny of Drake University, USA, reviewed a highly flexible *B*-spline *R*-matrix (BSR) method that has some advantages compared to the standard *R*-matrix (close-coupling) approach. The two essential refinements are i) the removal of orthogonality restrictions, which allows for the use of non-orthogonal orbital sets to represent both the bound and continuum one-electron orbitals, and ii) the use of *B*-splines as a universal and effectively complete basis to generate the *R*-matrix basis. There are several sources of uncertainties associated with this method. These include but are not limited to: 1) Errors in the structure description of the target states (energy levels, oscillator strengths, polarizabilities). 2) Errors associated with the cut-off in the close-coupling expansion, including inert subshells. 3) Approximations made in the treatment of relativistic effects. 4) Numerical approximations (integration/discretization schemes, use of an R-matrix box to account for exchange and full correlation only inside the box, etc.). Similarly to experiment, it is very difficult (if not impossible) to estimate systematic errors. The uncertainty generally depends on several factors, such as the quantity of interest (rate coefficient, integrated cross section, differential cross section, specific transition, energy, etc.).

CONVERGENT CLOSE-COUPLING CALCULATIONS FOR ELECTRON-ATOM AND ELECTRON-MOLECULE SCATTERING

Prof Fursa of Curtin University, Australia, reviewed the Convergent Close-Coupling (CCC) method which represents the infinite number of target bound states and its continuum via a finite number of states obtained by a diagonalization of the target in a square-integrable (Sturmian) one-electron basis. The possible sources of uncertainties in this method are numerical issues related to the solution of the close-coupling equations, accuracy of the calculated target wave functions, partial-wave expansion and the size of close coupling expansion. A fully relativistic formulation for the description of both the target structure and the collision process may be required for collisions with heavy atoms and molecules. Ways to estimate uncertainties of CCC method were proposed.

2.4 Methods in Electron-Molecule Collisions

CALCULATION OF DISSOCIATIVE ELECTRON ATTACHMENT CROSS SECTIONS

Dr Haxton of Lawrence Berkeley National Laboratory, USA, presented cross-sections of dissociative electron attachment (DEA) process employing the complex Kohn electron-molecular scattering method. The “Kohn Suite” consists of scattering codes coupled to MESA, a flexible electronic structure code from LANL (no longer maintained). The DEA process is described by two steps and the calculation of first step (attachment) is relatively easy. The calculation of the second step (dissociation) may be very difficult due to strong competition between dissociation ($AB^- \rightarrow A^- + B$) and autoionization ($AB^- \rightarrow AB + e^-$). The uncertainty in DEA cross-section depends upon the survival probability given roughly by the ratio of DEA to vibrational excitation and prior knowledge of this ratio from experiment or theory should affect uncertainty in DEA cross-section.

CALCULATIONS OF ELECTRON-MOLECULE SCATTERING CROSS SECTIONS USING THE R-MATRIX METHOD

Prof Gorfinkiel of Open University, UK, reviewed UK R-matrix method used to solve the electronic part of the electron-molecule scattering problem and presented sources of uncertainties associated with the method. Leaving aside the uncertainties associated with both the approximations used (Born-Oppenheimer, Fixed-Nuclei, etc.) and those linked to the numerical procedures employed, the quality of the cross sections depends strongly on the number of electronic states included in the calculation and the quality of the wave function. The uncertainty in the wave functions (target and target+scattering electron) is hard to ascertain. One could look at using a range of basis sets to study a specific target in order to estimate how much some calculated quantity (energy, permanent dipole and/or quadrupole moment) changes with basis set. Comparison of results calculated with different methods could be another way of looking at the precision of our results.

ELECTRON COLLISIONS WITH MOLECULAR IONS

Prof Lucchese of Texas A&M University, USA, reviewed theoretical methods for computing electron molecule collision based on single-center expansions and Schwinger variation expression. Three categories of uncertainties were described: uncertainties due to the physical model of the fixed nuclei approximation, uncertainties due to truncations of the N-electron close-coupling expansion and uncertainties due to truncations in the one-electron wave function expansion. Considered were methods to quantify these uncertainties such as sensitivity studies on the choice of radial and angular grids, convergence with respect to increasing one-electron basis set and the convergence of cross-sections with respect to the levels of correlation. A consistency test comparing different forms of the theory which should yield the same results, was proposed for photoionization cross-sections.

UNCERTAINTIES IN CALCULATIONS OF LOW-ENERGY RESONANT ELECTRON COLLISIONS WITH DIATOMIC MOLECULES

Prof Houfek, Charles University in Prague, Czech Republic, presented a model for nuclear dynamics of electron-molecule collisions using the fixed–nuclei calculations. A theoretical description of the dynamics of the molecular motion usually comprises two steps. First, quantum-chemical calculations of potential energy surfaces where molecular species are bound are performed and the second step involves calculation of the vibrational dynamics on these potential energy surfaces within an appropriate approximation. He identified uncertainties associated with 1) potential energy curves (surfaces), 2) fixed-nuclei electron scattering and 3) model for nuclear dynamics. Models for nuclear dynamics can be constructed with the local complex potential approximation or non-local, complex and energy-dependent potential. It is proposed to use a two-dimensional and simple model of electron-molecular collisions to estimate associated with the approximation.

LOW-ENERGY ELECTRON SCATTERING DATA FOR CHEMICAL PLASMA TREATMENT OF BIOMASS

Prof Lima of Instituto de Fisica Gleb Wataghin, Universidade Estadual, Brazil, presented the Schwinger variational method used to study molecular dissociation through electronic excitation. Sources of uncertainties were discussed in terms of controllable or uncontrollable. For example, the source of uncertainties associated with the free-particle Green’s function used in the Lippmann-Schwinger integral equation is controllable as well as L^2 expansion or N+1 wave function expansion. Uncertainties of the channel coupling operator and target description are rather uncontrollable. Multichannel effects on electronic excitation by electron impact were presented.

DEVELOPMENT OF A PROCEDURE FOR THE UNCERTAINTY EVALUATION IN THEORETICAL CALCULATIONS OF CROSS SECTIONS AND RATE COEFFICIENTS

Prof Kokoouline of University of Central Florida, USA, presented a procedure to estimate uncertainties of cross-sections in a systematic manner. The approach developed for nuclear data evaluation was applied to the problem of theoretical determination of cross sections in electron-molecule collisions using Hyper-Spherical method. The approach allows an evaluation of the uncertainty of final theoretical cross sections if uncertainties of all parameters used in the model are available. When input parameters of the theoretical model are correlated, the correlation reduces uncertainties of the final cross section. It also allows to account for the experimental data and uncertainties (if they are available) using the Bayesian analysis. The approach is general enough to be used for different atomic and molecular processes.

3. Technical Discussions

Three sessions were organized to discuss issues associated with quantifying uncertainties of calculated electron-atom, electron-molecule and heavy-particle collisional data. Discussions were led and summarized by Prof Bartschat, Prof Tennyson, and Prof Schultz for electron-atom, electron-molecule and heavy particle collisional data, respectively. Prof Schultz also gave a presentation on “Comments on Heavy-Particle Collision Data Assessment; General Discussion”, which is available at http://www-amdis.iaea.org/meetings/ITAMP/.

3.1 Uncertainty Estimates of Theoretical Electron-Atom Collision Data

Interested Groups

It seems as if the guidelines for Physical Review A (see Gordon Drake's discussion of the Editorial) are not really the same as for the IAEA and plasma modelers. Phys. Rev. A expects error estimates, for example, when the authors claim "high precision" or if "new physics" is predicted. This may apply to essentially any observable, target, projectile, energy, angle, spin etc. The IAEA and plasma modelers, on the other hand, are mostly interested in parameters that "matter", in the sense that changing them, for example, in a collisional radiative model (CRM), changes the outcome of that model to a significant extent. This reduces the requirement for error estimates in the practical sense, basically to large absolute cross sections and oscillator strengths and, in some cases, phases of the corresponding matrix elements (c.f. Yuri Ralchenko).

It was suggested (with no serious opposition) that we would concentrate on error estimates that are of most interest for the IAEA at this point.

Sources of Errors/Uncertainties

There are a number of possible sources of errors and uncertainties. Similar to experiment, it is very difficult (if not impossible) to estimate systematic errors, and most of those listed below fall into that category. It is also important to realize that the uncertainty generally depends on several factors, such as the quantity of interest (rate coefficient, integrated cross section, differential cross section). Also important is the type of transition (dipole-allowed, dipole-forbidden but with a direct contribution, exchange only) and, of course, the collision energy. Perturbative methods, in particular, are often limited to intermediate to high energies (several times the ionization threshold), they are most reliable for optically allowed transitions, and they are frequently used to "top up" the results when partial waves with high angular momenta are required.

Below is a list (no claim of completeness is being made) of important sources of errors and, consequently, resulting uncertainties:

- Since a target description for N electrons is a prerequisite for a collision calculation involving N+1 electrons, errors in the N-electron structure (energy levels, oscillator strengths, polarizabilities) can be expected to propagate into the collision problem.
- Errors associated with the cut-off in the close-coupling expansion, or the use of a perturbative method (plane-wave, distorted-wave to first or second-order).

- Approximations made in the treatment of relativistic effects.
- Numerical approximations (e.g., integration/discretization schemes, use of an R-matrix box to account for exchange and full correlation only inside a box, etc.)

Addressing and Estimating Errors/Uncertainties

Below are a few suggestions that may help in estimating the uncertainties or, even better, almost eliminate them for the cases of practical interest. Unfortunately, some of these suggestions may be impractical in reality, due to the requirement of both human and computational resources and the associated costs. Also, we need to make the assumption of "no bad surprises", i.e., currently unknown effects that may be of sufficient importance to change the outcome to the extent that they "matter" for the IAEA and plasma modelers. More specifically, small changes in energy levels that cannot be explained by existing theory may indicate some "new physics" and, consequently, will be scrutinized very carefully before being accepted for publication in Physical Review. On the other hand, chances are that these changes would not really matter for the purposes for plasma modeling.

Below are a few items that should be considered in uncertainty estimates, in particular regarding electron-atom collisions, where such estimates seem more realistic than for the more complex processes of electron-molecule and heavy-particle collisions:

- Purely numerical errors (space and time mesh, partial-wave convergence, etc.) should be negligible for "expert users". They can, and should be, checked carefully enough to convince any users of the published data that these results do not suffer from such problems.
- Structure problems are real, but they can, and should be, accounted for to the extent possible. For example, experimental energy levels are almost always more accurate than theoretical ones (at least more accurate than those used in subsequent collision models), and this also often holds for oscillator strengths, in particular for the strong transitions that "matter". Consequently, to minimize the errors in the structure description, experimental energy levels should be used if at all possible, and results for optically allowed transitions should be rescaled to ensure the correct high-energy behavior, which is effectively determined by the optical oscillator strengths.
- The importance of relativistic effects can be tested by performing calculations in different models: non-relativistic with angular-momentum recoupling into a relativistic scheme; semi-relativistic (Breit-Pauli); and full-relativistic (in practice Dirac-Coulomb).
- Convergence checks of the close-coupling expansion, including the systematic use of pseudo-states to account for coupling to the ionization continuum.
- Suitability checks of (likely) more approximate methods by checking the matching of their predictions to those from (likely) more accurate methods. Examples may include switching from close-coupling to distorted-wave at certain energies and certain angular momenta in the close-coupling expansion. The quality of the match should give some indication about the reliability of the method.
- Comparison with experiment. While this may look like the obvious approach, it requires a realistic estimate of the experimental uncertainty. Especially for state-to-state transitions in complex neutral targets, the availability of such data is rare, and there are numerous examples in the literature where the data seem questionable.

Current status regarding the cross sections that "most likely matter"

As mentioned above already, before making such a statement one would need to define "most likely" and "matter". One could try something like "most likely" meaning "covering 90% of the cases" and "matter" based on some sensitivity analysis of the plasma community. Below are suggestions (by the discussion leader) for electron collisions with the valence (outer) electrons. This might be achievable by using convergent close-coupling (CCC), R-matrix with pseudo-states (RMPS), and time-dependent close-coupling (TDCC) for low and intermediate energies and angular momenta, plus distorted-wave approaches to cover intermediate to high energies and angular momenta if a match of acceptable quality (see above) can be achieved.

- H: 3%
- He: 5%
- e-alkalis: light (Li, Na, K) – 10%, heavy (Rb, Cs) – 20%
- quasi-two electrons: light (Be, Mg, Ca) –10%; heavy – 30%
- noble gases other than He: (Ne, Ar)–20%, (Kr) – 30%, (Xe) – 40%
- open-shell atoms: light –30%; heavy such as Fe, W– too difficult to specify at this time
- isoelectronic positive ions to the above: same or better than neutrals

It should also be mentioned that some "special-purpose methods", such as the "polarized orbitals" approach or the closely related "static exchange plus polarization" method may be very accurate for elastic scattering below the first excitation threshold. This is supported by experimental data, which are likely very accurate for the one-channel case. Furthermore, the "Binary Encounter Bethe" (BEB) approach has been highly successful for ionization processes.   While a general estimate of the uncertainty is difficult for BEB, many of its predictions agree well with experimental data that, in turn, also seem rather accurate.

Next steps

In order to either confirm, reject, or improve the above estimates, it seems advisable to agree on further benchmark studies. Examples that came to mind are electron collisions with H, He, Be^+, Be, C, Ne^{4+}, Ne, ...), but no clear agreement was reached. A major reason for the lack of commitment is likely the perceived difficulty of getting such studies funded in the current research environment.

Conclusion

There is no doubt that estimates of uncertainties for theoretical results should be provided, both in the original publication and in tables that may go into the various databases. Unfortunately, it is unlikely that funding agencies that support fundamental research will provide the funds needed to perform extensive studies, and hence these funds would have to come from the interested parties. Until that happens, the best we can do is encourage our colleagues to do what they can, for example, in regard to the items listed above.

3.2 Uncertainty Estimates of Theoretical Electron-Molecule Collision Data

The most important molecular processes for (fusion) plasma modelling occur at low impact energies that are below the threshold electron impact ionization. This process is very well treated by Kim’s BEB model. Below this threshold there are a number of processes that need to be considered, namely: Elastic scattering (and momentum transfer), rotational excitation, vibrational excitation, Dissociative recombination or Dissociative attachment, electronic excitation and Impact dissociation.

Usually elastic scattering and electronic excitation (which is the usual route to impact dissociation) calculations are performed within the fixed nuclei approximation. While rotational excitation, vibrational excitation and dissociative recombination /attachment all require specially developed methods for treating nuclear motion effects. One consequence is that these calculations are never checked for consistency between the individual partial cross sections and the total cross sections. Furthermore calculations very rarely produce complete cross section sets.

Electron molecule calculations are performed for a variety of reasons. Traditionally they were used to model and interpret experiment. In this case it is necessary to demonstrate the validity and the limitations of the theoretical procedure used. However they are becoming increasingly used to provide primary data for databases on processes which are difficult to measure or cannot be measured experimentally. Given the decrease in the number experimental groups undertaking this work and the increasing demand for cross sections, the demand for theoretical data will continue to increase. Many databases, such as BASECOL (for astrophysical processes) and Phys4Entry (for space-craft re-entry), include either only or substantially theoretical data for electron collisions processes. For fusion plasmas, the need for data on processes involving tritium containing molecules (and ones containing Be) will only be satisfied by concerted theoretical efforts. It is essential that some sort of uncertainty estimates is attached to these data.

Uncertainties in electron-molecule collision calculations arise from three separate sources: target model, scattering model and the code/theoretical formalism used to implement them.

Concerning target studies:

Dipoles moments are important for elastic scattering and rotational excitation of polar molecules, and for optically allowed transitions in all molecules. It is straightforward to estimate uncertainties in dipole moments by systematic theoretical studies (for instance using the focal point method) and/or comparison with measurement. We would recommend that this should be done routinely.

For electronic excitation, uncertainties in the computation of electronic excitation energies can be studied using similar procedures although there is evidence that, except in the threshold region, inaccuracies in these energies is not the biggest source of error in the electronic excitation calculations.

The biggest issue involving the target is the quality of the target wavefunctions used in the calculation. For photoionization calculations, comparison of length and velocity calculations can be used to assess this. Unfortunately this option is not available for scattering calculations, so the only option is repeating calculations with different target wavefunctions to gauge the sensitivity to this aspect of the computational model.

Scattering models

Scattering models are usually the major source of (unquantified) uncertainty in electron scattering calculations. It is hard to suggest a rigorous solution to this problem but repeat calculations with variations on the model used can provide some information on this. The most promising approach is probably represented by systematic studies using pseudo-state methodology. It would be helpful to have some benchmark studies on a number of exemplar problems since the characteristics of collisions with different targets differ. At least one should consider electron collisions with a non-polar target and polar one. At this stage it would be advisable to do this for diatomic molecules whose nuclear motion is amenable to a thorough treatment. N_2 would seem to be one good choice as it is important for atmospheric and fusion studies, and there are many measurements available.

Formalism, codes, and numerical approximations

Formalism, codes, and numerical approximations are routinely discussed in papers, sometimes at some length. However inter-comparison between major codes such the R-matrix (UKRMol), Schwinger and Kohn codes suggest that these implementations give very similar results for the same model. Furthermore numerical approximations (grids, basis set truncation, etc) are generally well-understood and do not appear to be a major source of error, although it always helpful if uncertainties arising from this aspect of any calculation is quantified.

3.3 Uncertainty Estimates of Theoretical Heavy Particle Collision Data

Motivation

Detailed knowledge regarding heavy-particle collisions is essential for modeling and for experimental diagnosis of fusion plasmas, as well as for use in other applications such as astrophysics, plasma processing of materials, and heavy-ion treatment of disease. These collisions include a wide range of instances such as one- or few-electron collisions (e.g., H^+, He^{2+} + H with impact energies from the eV to MeV range) or many-particle collisions (e.g., particle-surface interactions). Data for the few-electron systems is required for modeling of momentum, energy, and particle transport in plasmas and for diagnostics such as charge exchange recombination spectroscopy or beam emission spectroscopy. Particle-surface interaction data are needed for understanding the vitally important interface of fusion plasmas with material bounding surfaces in order to understand surface erosion, contamination of the plasma with deleterious species, tritium retention, and particle recycling, for example. The accuracy and completeness of heavy-particle collision data is therefore a foundation of ongoing and future research and development of fusion energy. Furthermore, quantification of the uncertainty of the existing data for heavy-particle collisions, and that of new data produced, is necessary in order to assess the uncertainty of the models and diagnostics which rely upon them.

Background

Since the heavy-particle collision data that has been created over many decades, and for a variety of purposes most frequently outside of the consideration of the needs for data for fusion, is of varying uncertainty, historically a process has been adopted of (i) creating a comprehensive bibliography of all relevant publications or other sources of heavy-particle data, (ii) collection and compilation of data by atomic data centers or individual researchers or groups, and (iii) evaluation of the data for conformance with expected physical behaviors and inter-comparison amongst theoretical and experimental results. For instances in which a large number of results exist, this methodology allows quantification of uncertainty of the recommended result to a certain extent. For cases in which only a single data set exists, often the case where a very large, detailed tabulation of data such as cross sections or density matrix elements is needed, such an approach is largely not applicable.

Evolution of needs and capabilities

As fusion modeling and diagnostics have evolved to the present state-of-the-art in which higher accuracy and greater completeness of data sets is required, there has grown the need to better understand the uncertainty of theoretical data based on (i) the level of the model being solved (e.g., have approximations such as perturbation theory or classical electron dynamics been used or is the many-particle Schrödinger equation being solved directly) and (ii) the numerical accuracy of the solution. This comes at a time when fewer and fewer experimental activities are in existence, needed as important tests of theoretically produced data, and when the principal areas of theoretical interest in atomic physics have shifted to other applications such as ultracold gases, quantum information science, and precision measurements. Fortunately, even with fewer experimental or theoretical efforts being supported, theoretical techniques and computational power have reached the point where a greater number of heavy-particle collisions can be treated with demonstrably convergent methods.

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.

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.

- The need will also persist (and in some cases be crucial to fusion energy development efforts) for heavy-particle data that will not in the near term, despite rapid and significant progress in theoretical and computational methods, be amenable to demonstrably convergent solution of the most fundamental dynamical equations, and will require close collaboration with plasma experiments for quantification of uncertainty.
- Finally, there is the challenge to engender recognition of the special need for atomic, molecular, and optical data production, collection, evaluation, and dissemination for long-term support, critical to other fields in addition to fusion, requiring its own sustained community of experts.

4. Conclusions and Recommendations

The meeting was highly successful in exchanging ideas on sources of uncertainties associated with various theoretical methods used to calculate atomic and molecular data. There was a consensus that the theoretical atomic and molecular data community should be encouraged to include uncertainty estimates in calculated data. It was noted that uncertainty quantification (UQ) research is a good source of discovering a new kind of science. For example, a covariance matrix of input parameters has not been investigated and it may open a way for useful insights on theoretical method.

Currently, the *definition* of what an uncertainty of calculated data is and the *methodology* of how to measure or estimate the uncertainty of calculated data are not well known in this community. Terminologies used for UQ are well established in other areas in engineering and sciences by mathematicians and they need to be distributed to this community. The methodology how to deal with UQ is not unique and depends on applications. Unfortunately this field is lacking such tools. There are efforts to apply Baysian and Monte-Carlo methods for treating the random uncertainties of theoretical atomic and molecular data, but they need substantial development and refinement to be used in this field.

Roughly speaking, there are two different types of uncertainties in any theoretical atomic and molecular data: convergence and models. It is emphasized that at least the numerical uncertainties should be removed in the calculation and the convergence with the size of the basis sets should be carefully investigated. For heavy-particle collisions there is no standard code or *ab initio* code, only codes combined with various types of models. The uncertainties of models should be investigated.

While it is urgent to develop the method of prospective analysis, which is to be applied to newly calculated data sets, it is equally important to develop the method of retrospective analysis applied to existing data especially heavily used by plasma modelers. For example, the proposed method for electron-atom collisional data in Section 3.1 that certain types of calculated data may be regarded with a range of pre-determined uncertainties may be suitable for such retrospective analysis.

Developing a method to extrapolate quantitative estimates of uncertainty ranges based on empirical knowledge to the newly generated data is desirable. Extrapolating uncertainty ranges will not be valid for theoretical data of all processes. However, certain types of data may be assigned uncertainties by extrapolation from known sources; a good example is the line strength data of atomic transition. With a well-defined extrapolation method, the number of reference sets will grow large and fast by combining the limited number of high precision experiment and a good number of high precision theoretical data.

In the mid 1970s and 1980s, the CHIANTI and ADAS databases took a different path to build data sets for astrophysical plasmas. CHIANTI database focused more on evaluation while ADAS database on completeness of data sets. For user community, complete data sets are often preferred, however, later on, high quality data becomes on demand. In order to produce comprehensive and recommended data, a coordinated effort from the data producing community is essential.

There should be a database devoted to the standard reference or evaluated and recommended database for fusion applications. The ALADDIN database maintained by IAEA atomic and molecular unit started as a database of evaluated and recommended data in the 1980s and 1990s. In recent years, the focus has changed from evaluation to dissemination and the current ALADDIN database contains many un-evaluated data sets. The Unit should increase evaluation activities for the ALADDIN database. In particular, 30-year old recommended data in ALADDIN should be re-evaluated with the most up-to-date data.

Finally, funding for the UQ research is still problematic in atomic and molecular data community, although it is increasing in other areas of science and engineering. The fusion community needs to motivate theoretical data producers if uncertainties associated with data are required for their applications. Studies of sensitivity analysis of A&M data to results of a global model will be valuable in recognizing the most important data sets that matter, and hence prioritizing them for UQ investigation with the limited resources available.

List of Participants

Connor P. Ballance, Auburn Univ. AL, USA, ballacp@auburn.edu

James F. Babb, ITAMP, MA, USA, jbabb@cfa.Harvard.edu

Klaus Bartschat, Drake University, USA, klaus.bartschat@drake.edu

Hyun-Kyung Chung, IAEA, h.chung@iaea.org

James P. Colgan, Los Alamos Nat'l Lab, NM, USA, jcolgan@lanl.gov

Attila G. Csaszar, MTA-ELTE, Budapest, Hungary, csaszar@chem.elte.hu

Gordon W.F. Drake, University of Windsor, Ontario, Canada gdrake@uwindsor.ca

Christopher J. Fontes, Los Alamos Nat'l Lab, NM, USA, cjf@lanl.gov

Dmitry Fursa, Curtain University, Australia, d.fursa@curtin.edu.au

Jimena D. Gorfinkiel, The Open University, Milton, keynes, UK, j.gorfinkiel@open.ac.uk

Daniel J. Haxton, Lawrence Berkeley National Laboratory, CA, USA, djhaxton@lbl.gov

Karel Houfek, Charles University in Prague, Czech Republic, karel.houfek@mff.cuni.cz

Tom Kirchner, York University, Canada, tomk@yorku.ca

Viatcheslav Kokoouline, University of Central Florida, FL, USA, Viatcheslav.Kokoouline@ucf.edu

Alexander Kramida, National Institute of Standards and Technology, MD, USA, alexander.kramida@nist.gov

Predrag Krstic, Stony Brook University NY, USA, predrag.krstic@stonybrook.edu

Marco Aurelio Pinheiro Lima, Instituto de Fisica Gleb Wataghin, Universidade Estadual, Brazil maplima@ifi.unicamp.br

Robert Lucchese, Texas A&M University, TX, USA lucchese@mail.chem.tamu.edu

Luis Mendez, Universidad Autónoma de Madrid, Spain, l.mendez@uam.es

Yuri Ralchenko, National Institute of Standards and Technology, MD, USA, yuri.ralchenko@nist.gov

Detlev Reiter, Forschungszentrum Juelich GmbH, Germany, d.reiter@fz-juelich.de

David R. Schultz, University of North Texas, TX, USA, david.schultz@unt.edu

Al Stauffer, York University, Canada, stauffer@yorku.ca

Jonathan Tennyson, University College London, UK, j.tennyson@ucl.ac.uk

Oleg Zatsarinny, Drake University, USA, OlegZatsarinny@drake.edu

Appendix 2

Joint IAEA-ITAMP Technical Meeting
Uncertainty Assessment for Theoretical Atomic and Molecular Scattering Data

Institute of Theoretical Atomic, Molecular and Optical Physics, Cambridge, MA, USA

7-9 July 2014

Agenda

Monday, 7 July — Phillips Auditorium

08:30	***Registration, Coffee and Pastries***
Session I	***Chair: Jim Babb***
09:00 - 09:05	***Welcome (ITAMP)***
09:05 - 09:20	**Hyun-Kyung Chung (IAEA),** *"Meeting Objective"*
09:20 - 10:00	**Gordon Drake,** *"Uncertainty Estimates: A new Editorial Standard"*
10:00 - 10:40	**Tom Kirchner,** *"Heavy-particle collisions involving many active electrons: how (in-) accurate are our calculated cross sections?"*
10:40 - 11:10	***Break***
11:10 - 11:50	**Predrag Krstic,** *"Sensitivity, Error and Uncertainty Quantification: InterfacingModels at Different Scales"*
11:50 - 12:30	**Luis Mendez,** *"Uncertainties of electron capture cross sections in* Be^{4+} + *H(1s) collisions"*
12:30 - 14:00	***Lunch***
Session II	***Chair: Klaus Bartschat***
14:00 - 14:40	**Conner P. Ballance,** *"The propagation of correlated uncertainties from theoretical collisional calculations through to plasma spectral diagnostics"*
14:40 - 15:20	**James Colgan,** *"Time Dependent Close Coupling Methods for Electron Atom/Molecule Scattering"*
15:20 - 15:50	***Break***
15:50 - 16:30	**Al Stauffer,** *"An Evaluation of the Accuracy of the Relativistic Distorted Wave Approximation for the Calculation of Cross Sections for the Excitation of Atoms by Electron Impact"*
16:30 - 17:10	**Oleg Zatsarinny,** *"Benchmark calculations for electron collisions with complex atoms"*
17:10 - 17:50	**Dmitry Fursa,** *"Convergent Close Coupling Calculations for ElectronAtom/Molecule Scattering"*
18:00	***Reception (Perkin Lobby)***

Tuesday, 8 July

Session III	***Chair: Jonathan Tennyson***
08:00	***Coffee and Pastries***
08:30 - 08:50	***David Schultz , "Heavy Particle Collisions"***
08:50 - 09:30	**Heavy particle Discussion,** *Discussion Leader: David Schultz*
09:30 - 10:10	**Attila Csaszar**, *"Uncertainties of Molecular Structural Parameters"*
10:10 - 10:40	***Break***
10:40 - 11:20	**Daniel Haxton,** *"Calculation of dissociative electron attachment cross sections"*
11:20 - 12:00	**Jimena D. Gorfinkiel,** *"Calculations of electronmolecule scattering cross sections using the Rmatrix method"*
12:00 - 12:40	**Robert Lucchese**, *"Electron Collisions with Molecular Ions"*
12:40 – 13:40	***Lunch***

Session IV	***Chair: James Colgan***
13:40 – 14:20	**Karel Houfek,** *"Uncertainties in calculations of low-energy resonant electron collisions with diatomic molecules"*
14:20 – 15:00	**Marco Lima**, *"Low energy electron scattering data for chemical plasma treatment of biomass"*
15:00 – 15:40	**Viatcheslav Kokoouline,** *"Development of a procedure for the uncertainty evaluation in theoretical calculations of cross sections and rate coefficients"*
15:40 – 16:00	***Break***

Wednesday, 9 July

Session VI ***Chair: Hyun -Kyung Chung***

08:00	***Coffee and Pastries***
08:30 – 09:10	**Detlev Reiter**, *"Status of database and data analysis for fusion edge plasma transport studies*”
09:10 – 09:50	**Yuri Ralchenko,** *"Data quality and needs for collisional-radiative modeling"*
09:50 – 10:10	**Alex Kramida**, *Assessing Uncertainties of Theoretical Atomic Transition Probabilities with Monte Carlo Random Trials*
10:10 – 10:40	***Break***
10:40 – 11:20	**e-Atom Discussion**, *Discussion Leader: Klaus Bartschat*
11:20 – 12:00	**e-Molecule Discussion**, *Discussion Leader : Jonathan Tennyson*
12:00 – 12:30	IAEA Discussion and Conclusions, Hyun-Kyung Chung
12:30	***Meeting Adjourn***
12:30 – 14:00	***Lunch***
14:00 – 16:00	Time for open or follow-on discussions

Abstracts and Summaries of Presentations

UNCERTAINTY ESTIMATES: A NEW EDITORIAL STANDARD

GORDON W.F. DRAKE

University of Windsor, Canada, and Editor of Physical Review A

The objective of achieving higher standards for uncertainty estimates in the publication of theoretical data for atoms and molecules requires a concerted effort by both the authors of papers and the editors who send them out for peer review. In April, 2011, the editors of *Physical Review A* published an Editorial announcing a new standard that uncertainty estimates would be required whenever practicable, and in particular in 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.

The new policy means that papers that do not meet these standards are not sent out for peer review until they have been suitably revised, and the authors are so notified immediately upon receipt. The policy has now been in effect for three years.

HEAVY-PARTICLE COLLISIONS INVOLVING MANY ACTIVE ELECTRONS: HOW (IN-)ACCURATE ARE OUR CALCULATED CROSS SECTIONS?

TOM KIRCHNER

Department of Physics and Astronomy, York University, Toronto, Ontario, Canada M3J 1P3

The theoretical description of ion-atom and ion-molecule collisions is a difficult task: one deals with a two-center or a multi-center problem, for which standard angular momentum expansions do not work very well, and one typically faces the problem that several processes, such as electron transfer and ionization into the continuum, compete with each other. If more than two electrons are present, the numerical solution of the full Schrödinger equation of the collision system is out of reach and assumptions and approximations have to be introduced at the outset. This is to say that one solves (at most) a model in order to describe the collision system and, as a consequence, has to deal with a two-fold problem when it comes to estimating the uncertainties and inaccuracies of the calculated data: (i) to assess the limitations of the model (which may be compared with quantifying systematic errors in an experiment); (ii) to perform careful convergence studies for the numerical procedures involved (which may be compared with narrowing statistical experimental errors).

These two interrelated problems were illustrated by using a recent work on X-ray emission from a highly-charged ion after electron capture as an example [1]. The calculations for this problem are based on the assumption that collisional capture and post-collisional de-excitation processes can be treated independently. This introduces a first systematic error, but probably a very small one, because capture and de-excitation take place on different time scales. Similarly, the assumption of a classical straight-line projectile trajectory is uncritical.

Three sources of significant uncertainties are present in the collision calculation: (i) usage of the independent-electron model, (ii) usage of a finite basis set to solve the single-electron time-dependent Schrödinger equation, (iii) usage of multinomial statistics to calculate multiple (shell-specific) capture probabilities, which form the starting point for the subsequent deexcitation calculation. It was argued that it is difficult to quantify the uncertainties associated with these three steps, but that qualitative information on the "error bars" associated with them can be obtained by using and comparing different model variants and approximations, i.e., different single-particle Hamiltonians for item (i), different basis sets for item (ii), and different multinomial formulae for item (iii). A few such variants were discussed, e.g., a "no-response" vs. a "target response" Hamiltonian and multinomial analyses based on orbital-specific versus orbital-averaged single-particle probabilities.

Further modeling is required for the post-collision dynamics, that is the de-excitation of the projectile ion after multiple capture. Simple Auger and radiative decay models were discussed and assessed once again by using and comparing slightly different versions of them.

The outcome of this procedure of varying the used models within reasonable bounds is not a unique answer, but rather a band of results for the observables of interest—in this case for the X-ray emission intensities for 1snp→1s2 transitions in Ar^{16+} ions after capture in 7 keV/amu collisions with argon atoms. It was suggested that in the absence of better methods for the quantification of uncertainties of calculated data one should interpret this band as the error bar of the calculation.

Similar ideas and methods have been used to study electron removal from (water and methane) molecules and the occurring subsequent fragmentation processes [2]. Not surprisingly, basis set convergence is a greater challenge for ion-molecule than for ion-atom collision problems, i.e., the statistical error is significantly larger. Nevertheless, also in this case it is possible to obtain a good qualitative sense of the uncertainty of a calculation by following the same strategy of varying the models used within reasonable bounds.

[1] A. Salehzadeh and T. Kirchner, J. Phys. B 46, 025201 (2013).

[2] T. Kirchner et al., Adv. Quant. Chemistry 65, 315 (2013).

SENSITIVITY, ERROR AND UNCERTAINTY QUANTIFICATION: INTERFACING MODELS AT DIFFERENT SCALES

PREDRAG S KRSTIC

Institute for Advanced Computational Science, Stony Brook University, NY 11790

Discussion on accuracy of AMO data to be used in the plasma modeling codes for astrophysics and nuclear fusion applications, including plasma-material interfaces (PMI), involves **many orders of magnitude of energy, spatial and temporal scales**. Thus, energies run from tens of K to hundreds of millions of K, temporal and spatial scales go from fs to years and from nm's to m's and more, respectively. The key challenge for the theory and simulation in this field is the consistent integration of all processes and scales, i.e. an "integrated AMO science" (IAMO). The principal goal of the IAMO science is to enable **accurate** studies of interactions of electrons, atoms, molecules, photons, in many-body environment, including complex collision physics of plasma-material interfaces, leading to the best decisions and predictions. However, the accuracy requirement for a particular data strongly depends on the **sensitivity of the respective plasma modeling** applications to these data, which stresses a need for immediate sensitivity analysis feedback of the plasma modeling and material design communities. Thus, the data provision to the plasma modeling community is a "two-way road" as long as the accuracy of the data is considered, requiring close interactions of the AMO and plasma modeling communities.

There is a lot of **subjectivity** in use of the glossary pertinent to the accuracy of the AMO/PMI data, which is an obstacle for consistent treatment of the **uncertainty quantification** (UQ) of the data. On the other hand, to have an effective and objective UQ one has to bring together physics, computer science and applied mathematics communities. Significant progress with this kind of multidisciplinary unification has been done in atmospheric/climate as well as in the material sciences, while the AMO/plasma modeling communities are just making the first steps in the AMO UQ science.

The generic meaning of the term "uncertainty" is the maximal deviation of the calculated or measured quantity from the true value of the relevant observable. By its source, the uncertainty can be **aleatoric and epistemic**. **Aleatoric** uncertainty is caused by the inherent randomness of a considered (calculated or measured) phenomenon. Being described by the probability distribution it cannot be eliminated. An example of this kind of uncertainty in PMI are width and depth of a layer of deuterium formed upon impact and thermalization cascade at the surface (of tungsten, carbon,, at ps times). Having in mind randomness in the dynamical surface microstructure, created through time by the bombardment by various drivers from plasma (various energies, angles, particles,…) and their synergy, almost all data in the PMI science are subject to aleatoric uncertainties. It is fair to say that the randomness in the plasma irradiation drivers is the driver of the aleatoric uncertainties at the PMI. In addition, these uncertainties evolve through the multiscales of time and space together with the observed phenomenon (for example diffusion on the mentioned deuterium layer at longer, micro/mili second times). Thus, any uncertainty of a calculated PMI quantity has to be defined as being specific for a particular time/space/energy scale.

The traditional trial-and-error approach to PMI for future fusion devices by successive refitting the walls of toroidal plasma devices with different materials and component designs is becoming prohibitively slow and costly. Need for the bottom-up approach necessarily starts from the fs-ps time, and nm space scales. At these scales the PMI processes are discrete, atomistic in nature. Thus, at the ITER typical flux of 10^{25} particles/m^2s, one particle impinges a typical modeling surface of 10 nm^2 each 10 ns. However, most of the processes at the PMI irradiated by the 100 eV (or less) particles (including the most complex chemical sputtering) require less than 50 ps for their evolution. Still, each impact from plasma meets a different target, "functionalized" by the previous impacts. An observed PMI phenomenon eventually reaches a "saturation" at the ns time scale, and this is when the simulation data have to be taken and reported. These all indicate a need for both a random cumulative-bombardment preparation of the surfaces as well as statistics (Monte Carlo irradiation of a surface element that could be tens of nm^2). If irradiation is performed by the plasma at fixed temperature, then the particle-driver known energy distribution in the simulation has to be included in the statistics of the trajectories. The response of the PMI uncertainty distribution does not follow the "linear superposition principle", and one of the expected outcomes of the development of the UQ mathematics for PMI is prediction of the probability distributions of a studied quantity in response to the known distribution of the plasma driver(s).

The **epistemic** uncertainty in the AMO computer simulations is caused by a lack of understanding or by incorrect knowledge on the phenomenon, characterized by use of insufficient number of parameters, or by the wrong or inaccurate parameters. Unlike aleatoric uncertainties, the epistemic uncertainties can be improved by the process of learning. An example of this kind of uncertainty, with huge consequences in PMI, is the TRIM (binary potentials) treatment of the damage production in bombarding a tungsten surface by self-atoms. Since TRIM doesn't follow the surface evolution upon bombardment it predicts unreasonable high DPAs (displacements per atom). A more correct treatment, with a use of classical molecular dynamics and multibody potentials, shows a strong recombination of the Frenkel pairs produced by each self-atom impact, leading to many orders of magnitude smaller DPA rates. Another example of epistemic uncertainty had been inappropriate use of classical molecular dynamics to predict erosion and hydrogen retention in lithiated carbon surfaces. Presence of lithium, that has low electronegativity in comparison to carbon, hydrogen, oxygen (tungsten and other fusion materials), causes a strong electric polarization of all neighboring atoms (and consequent long-range forces) which depends on the instantaneous coordinates. This effect, being dependent on the instantaneous electron cloud, cannot be treated by classical molecular dynamics - it has to include quantum mechanics. Only upon use of the quantum-classical molecular dynamics a correct agreement with experimental findings on the erosion and hydrogen retention was obtained, and explained by the lithium- residual oxygen far reaching polarizing interactions.

Typical for the fundamental, atomistic-scale processes in PMI is use of **molecular dynamics**, either classical or quantum-classical, depending on the system atomic configuration. Molecular dynamics is "as good as are the interatomic potential models" used. The calculated data may vary orders of magnitude by using different MD potentials. This contains another type, method-based, epistemic uncertainty – caused by inaccuracy of the potential energy surface (PES) in classical molecular dynamics. The development of the UQ mathematics to predict the sensitivity of the MD results to this kind of uncertainties is of high interest for the PMI simulations. The same can be stated for the pair potentials in a QCMD (SCC DFTB based), or uncertainties of the exchange-correlation functionals if DFT is used.

Of high importance in any uncertainty quantification is **validation** of the data. Only mutual validation of theory/simulation and experiment can build an effective multibody PMI science. So far, a remarkable agreement was obtained of theory and experiment whenever simulation can closely mimic a carefully executed experiment. This "mimicking" condition requires the simplified experiments in PMI, like are the beam-surface experiments. Although such experiments cannot reproduce synergy of the plasma drivers and respective PMI processes, these are a necessary "building stone" in decreasing the epistemic uncertainties in PMI simulations, through filling the holes in the knowledge of the phenomenology of the processes.

In conclusion, the accuracy of the PMI data need to be categorized with respect to the surface and projectile states, to various temporal and spatial scales, to the type of users, to the needed format of the particular phenomena, etc. – all of these are extremely difficult to reach. The requirement, needed for consistency in the integrated plasma-PMI modeling (also applicable to all AMO data) is obtaining all data and their uncertainties for a particular subsystem **"at the same footing"**, also very difficult to obtain. However, these two requirements are the necessary directions for obtaining comprehensive, **critically evaluated** and possible **recommended** data to the plasma community.

UNCERTAINTIES OF ELECTRON CAPTURE CROSS SECTIONS IN Be^{4+} + H(1s) COLLISIONS.

L. MÉNDEZ, CLARA ILLESCAS, ALBA JORGE, L. F. ERREA, I. RABADÁN AND J. SUÁREZ

Departamento de Química, Universidad Autónoma de Madrid (Spain)

We have considered one-electron systems where the theoretical methods are well established. The use of different computational alternatives enables the accurate evaluation of nl-partial cross sections in a wide range of collision energies. In the presentation we have analyzed the uncertainties of n-partial charge exchange (CX) cross sections in Be^{4+} + H(1s) collisions, which are relevant in tokamak plasmas and experimental data are not available.

In the energy range $1 \leq E \leq 100$ keV/u the semiclassical treatment is applied and the uncertainties associated to this approximation can be neglected. We have studied the results of four methods:

- The close-coupling molecular treatment (MOCC), where the electronic wavefunction is expanded as a linear combination of molecular orbitals of the BeH^{4+} quasimolecule. Large-scale calculations have been carried out by Errea *et al.* J. Phys. B **31**, 3527 (1998) and Harel *et al.* At. Data. Nucl. Data Tables **68**, 279 (1998).

- The close-coupling atomic treatment (AOCC), where the electronic wavefunction is expanded as a linear combination of atomic orbitals of H and Be^{3+}. AOCC calculations in a large basis set, including pseudostates, have been performed by Igenbergs *et al.* J. Phys B **42**, 235206 (2009).

- The classical trajectory Monte Carlo method (CTMC). New calculations have been carried out using the eikonal-CTMC of Illescas and Riera Phys. Rev. A, **60** 4546, (1999).

- The numerical integration of the time-dependent Schrödinger equation (Minami *et al.* J. Phys. B **39**, 2877 (2006)). New calculations have been performed using the GridTDSE program of Suarez et al. Comp. Phys. Commun. **180**, 2025 (2009).

All methods involve time and impact parameter integrations; the uncertainties associated to these numerical procedures are very small and have not been considered. To analyze the uncertainties of the calculations, we have considered three energies:

1. At low energies, E<10 keV/u, the most accurate and less cumbersome method is the MOCC treatment. The accuracy of the molecular expansion is mainly related to the size of the molecular expansion, since the basis functions are exact eigenfunctions of the electronic Hamiltonian and the common translation factor is not critical. In this respect, the common translation factor method is formally convergent, and a functional form of the translation factor that fulfills a few conditions improves the convergence speed of the expansion. The uncertainties of the cross sections can be estimated by carrying out calculations with different basis sets. Calculations at E = 1 keV/u show that the absolute uncertainties of total CX cross section and partial cross sections for population of Be^{3+}(n=3, 4) are smaller than 3×10^{-3} Å^2. The agreement with the AOCC calculation indicates that these cross sections are probably more precise, with differences between both calculations smaller than 1% .

2. At a collision energy of 30 keV/u, the AOCC is the most accurate method. The convergence study of Igenbergs *et al.*, together with the comparison with the GridTDSE calculation lead to a estimate of the relative uncertainty of about 1% for the total CX cross section and similar relative uncertainties for the cross sections for populating the main CX channels (n=3, 4). Similar absolute uncertainties obviously lead to high relative uncertainties in the cross sections for populating CX excited states (≈30% for n=6).

3. At E= 100 keV/u, target ionization is the dominant reaction. Besides, highly excited atomic levels are populated, which makes difficult to apply close- coupling methods. The precision of CTMC results can be related to the number of trajectories included, but false convergence is found for the population of low-n levels (Be^{3+} (n=2) in the present case), which is an intrinsic limitation of the method. The systematic uncertainty associated to this difficulty of the method can be obtained by comparing the results from calculations with different initial distributions. The total uncertainty of the total CX cross sections can be estimated in 1×10^{-3} Å^2 (≈3%). The main component of the uncertainty of the cross sections calculated with the GridTDSE method is the density of the grid employed to evaluate the electronic wavefunction. The CTMC and GridTDSE partial cross sections for production of Be^{3+} with $2<n<9$ differ in less than 0.03 Å^2 , which provides an additional estimate of the precision of both calculations.

In general, theoretical methods are able to provide high precision CX cross sections for one-electron systems, and the uncertainties can be estimated by means of a convergence study of the calculation. A similar situation is expected for collisions with one effective electron (e.g. C^{4+} + H). However, it is not easy to extend these ideas to many-electron systems, where high-energy calculations are often based on the application of the independent electron approximation. At low collision energies, the quality of the basis functions is critical in the description of many-electron collisions. Further investigation is also required for ion(atom)/molecule collisions.

THE PROPAGATION OF CORRELATED UNCERTAINTIES FROM THEORETICAL COLLISIONAL CALCULATIONS THROUGH TO PLASMA SPECTRAL DIAGNOSTICS

CONNOR P. BALLANCE

Department of Physics, Auburn University, Auburn, AL, USA

1. Encourage our respective communities, whether data producers, database managers or plasma modellers to support the concept of uncertainties on future calculations, where possible. It would be beneficial for this to receive for funding support for the various funding agencies, not excluding computer support at National Supercomputer Facilities, to ascertain meaningful uncertainties from many sample calculations.

2. We categorize the problem into 2 groups:

Baseline uncertainty data to give an indication of the parameter space. For practical purposes, this may the variation in collisional data already within the literature/ AMO databases. However, in the absence of available data, this could be the variation in quickly calculated non-perturbative methods, with different scattering potentials and/or the difference between two methods i.e. a plane-wave born and a distorted-wave calculation.

Method sensitivity uncertainty data with tighter and more realistic error bars, but within a single method.

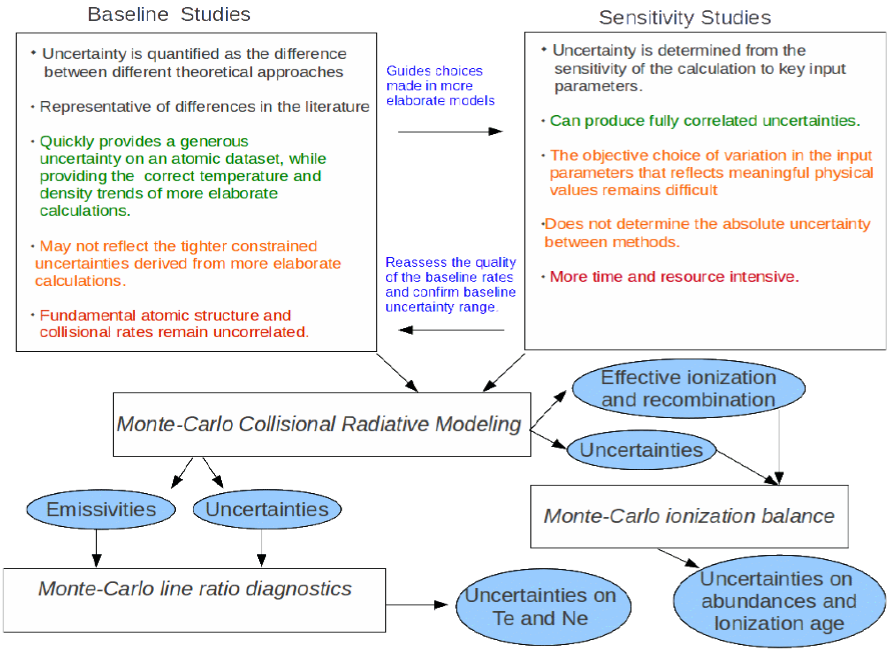
As a practical example, we may use the R-matrix method within a Monte Carlo context, to take say a 100-1000 structure calculations all the way through to a 100-1000 electron-impact excitation, ionisation, di-electronic recombination calculations. Using the resulting collisional rates, we can see how the variation in one collisional processes interacts with another to correlate the uncertainty, through to a diagnostic.

(see the attached Figure, for an assessment of the relative merits of each)

3. Our primary goal is not cross sections in isolation but rather how they interact to provide uncertainty in a magnetic fusion /astrophysical plasma diagnostic. I should state, that there was discussion on the final day as to whether putting error bars was the end of our responsibility or just the starting point to diagnostics with correlated uncertainty between different collisional processes.

4. I presented He-like O, as the example of the baseline approach to an astrophysical diagnostic.

5. For the baseline approach, some distribution to describe the variation of results must be chosen. I talked briefly about the simplicity of a Gaussian distribution, however a log-normal distribution has more physical meaning.



TIME-DEPENDENT CLOSE-COUPLING METHODS FOR ELECTRON-ATOM/MOLECULE SCATTERING

JAMES COLGAN

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA

The time-dependent close-coupling (TDCC) method centers on an accurate representation of the interaction between two outgoing electrons moving in the presence of a Coulomb field. It has been extensively applied to many problems of electrons, photons, and ions scattering from light atomic targets.

Theoretical Description

The TDCC method centers on a solution of the time-dependent Schrödinger equation for two interacting electrons. The advantages of a time-dependent approach are two-fold; one treats the electron-electron interaction essentially in an exact manner (within numerical accuracy) and a time-dependent approach avoids the difficult boundary condition encountered when two free electrons move in a Coulomb field (the classic three-body Coulomb problem).

The TDCC method has been applied to many fundamental atomic collision processes, including photon-, electron- and ion-impact ionization of light atoms. For application to electron-impact ionization of atomic systems, one decomposes the two-electron wavefunction in a partial wave expansion and represents the subsequent two-electron radial wavefunctions on a numerical lattice. The number of partial waves required to converge the ionization process depends on the energy of the incoming electron wavepacket and on the ionization threshold of the target atom or ion.

Sources of uncertainties

A typical TDCC calculation must be checked for convergence with respect to a number of different numerical parameters. The three most important of these are the extent and grid spacing of the radial mesh, the number of partial waves retained in the expansion, and the time for which the wavefunctions are propagated.

For light neutral atoms we have found that a radial mesh spacing of 0.1 or 0.2 atomic units (a.u.) is usually adequate to represent the bound wavefunctions and to perform an accurate solution of the partial differential equations. However, more recent applications that represent some of the inner orbitals of a multi-electron target on the radial mesh may require much finer mesh spacings to accurately represent the inner orbitals (for example, the 1s orbital of Mg). In such cases a smoothly varying radial mesh was found to be convenient. The extent of the radial mesh is usually taken to be around 100 a.u., although a larger mesh may be required for very low-energy collisions for which the electron-electron interactions take place over longer times.

The number of partial waves required to converge an ionization cross section will depend on the energy of the incoming electron wave packet. We have found that including up to L=10-15 is often sufficient to converge low and moderate energy collisions. Higher energy electrons will require larger number of partial waves. One must also ensure convergence with respect to the number of coupled channels that make up each partial wave.

One usually propagates the TDCC equations until the probability for ionization has reached a constant value (for a given partial wave). The time required to reach this condition will also be strongly dependent on the energy of the incoming wavepacket.

In all cases, one tends to monitor all of these convergence criteria before confidence is reached in a given ionization cross section. It is not uncommon to run multiple sets of TDCC calculations to ensure that the convergence with respect to all these parameters is reached. We also note that convergence is often more difficult to attain when ionization from excited states is considered.

The discussion above pertains to the numerical uncertainties inherent in a TDCC calculation. Usually an experienced user, given sufficient computational resources to fully check convergence, can minimize such uncertainties. However other uncertainties often exist in computed TDCC ionization quantities that are based on physics issues. For example, in the electron-impact ionization of neon, we have found that the interaction of the core electrons with the two outgoing electrons is important and exhibits strong term-dependence. The current implementation of the TDCC approach treats the interaction of the outgoing electrons with the core electrons in a configuration-average manner, and so one finds inaccuracy in the computed ionization cross section due to this physics issue. Such uncertainties are very difficult to gauge as they will in general be dependent on the energy of the incoming electron and the nature (i.e. the electron configuration) of the target species.

How to estimate uncertainties

We have found that a reasonable way to estimate uncertainties is to make detailed comparisons with other theoretical approaches, especially methods that, in principle, treat the electron-electron interaction rigorously via close-coupling expansions. Such comparisons have been made for electron-impact ionization cross sections from light atoms (for example, H through N). We have found variations in the ionization cross sections of (usually) less than 20%, which can be thought of as a first step in estimating the uncertainty of these cross sections. For heavier systems, the uncertainty is likely to be larger, since the more complex atomic structure and more involved interactions between the core and outgoing electrons makes close-coupling calculations significantly more difficult.

AN EVALUATION OF THE ACCURACY OF THE RELATIVISTIC DISTORTED-WAVE APPROXIMATION FOR THE CALCULATION OF CROSS SECTIONS FOR THE EXCITATION OF ATOMS BY ELECTRON IMPACT

ALLAN D. STAUFFER

York University, Toronto, Canada

1. The Relativistic Distorted-Wave (RDW) method uses the standard formula for the T matrix for electron-atom scattering except that the target wave functions and distorted-waves are obtained as solutions of the Dirac equations. Thus the target states have wave functions for each fine-structure level which depend on the total angular momentum J of the atom including distinct energies for each level. The high energy behavior of the integrated cross sections depends on the J values of the initial and final levels for the excitation in question. The target wave functions are Dirac-Fock configuration-interaction wave functions obtained from the GRASP2K code and as such can reach arbitrary accuracy if enough configurations are included. Both the T-matrix and the Dirac equations for the distorted waves contain non-local exchange terms. The method is valid for incident electron energies exceeding two to three times the threshold value. Thus for excitation from the ground state of the noble gases, the method is applicable for incident energies of about 25 eV and above, less so for excitation from excited states where the threshold is smaller. Unitarization of the resulting cross sections would lower the energy at which this method is valid but would require an extensive set of cross sections, including elastic scattering from all of the levels included in the calculation of the target states.

2. The numerical methods used to obtain the target states, the distorted waves and the T-matrix elements are accurate to at least one part in 10^6, well beyond the expected accuracy of the resulting cross sections. The method is valid for higher energies and does not give reliable cross sections near threshold and does not include any resonance behavior. Focusing on integrated cross sections, we note that for excitations where the direct term of the T matrix is non-zero, the majority of the contribution to the cross section comes from the forward scattering peak in the differential cross sections. For excitations which are solely due to the exchange of the incident electron with one of the bound target electrons, i.e. where the direct term of the T matrix is zero, significant contributions to the integrated cross section come from the whole angular range of scattering. The major source of uncertainty beyond the limitations of the method is the quality of the target wave functions themselves. In principle, these wave functions can be obtained from the GRASP2K code to arbitrary accuracy by including more states in the configuration-interaction description of the target. In practice, we are limited to a finite set of the most important configurations describing the target states.

3. The magnitude of the differential cross section for scattering at zero degrees is proportional to the optical oscillator strength calculated in the length formulation for the transition in question. (Note that in the discussion of my presentation, it was erroneously stated that the magnitude of the cross section was proportional to the square of the optical oscillator strength). Thus in order to ensure a correct magnitude of the integrated cross sections, the oscillator strength for the transition must be accurate. Extensive tables of experimental optical oscillator strengths for allowed transitions between fine-structure levels are available through the error estimates can be rather large. This detailed information provides another justification for the relativistic treatment of these electron excitation processes.

There are much less data available for direct excitations corresponding to transitions which are not optically allowed. One way to deal with this situation is to include intermediate levels in the description of the target wave functions which yield allowed optical oscillator strengths involving either the initial or final states of the excitation. (Note that the GRASP2K code produces these oscillator strengths as part of the calculations). Obtaining accurate values for both types of transitions indicates the accuracy of the target wave functions themselves.

There are other indicators of the accuracy of the target wave functions, such as the agreement between the length and velocity forms of the oscillator strengths, the energies of the various fine-structure levels and the correct energy ordering of these levels. Note that the geometric average of the length and velocity forms of the oscillator strength provides a result independent of the energy difference between the initial and final states of the transition, thus removing the influence of the errors in the calculated energy difference. However, it is the value of the oscillator strength in the length form that is proportional to the cross section and thus determines the accuracy of the final result.

This test of accuracy does not directly apply to excitations proceeding via exchange. However, obtaining accurate oscillator strengths involving the initial and final states of such excitation gives some confidence that the resulting cross section will be reliable. Nevertheless, the errors in such cross sections are likely to be larger in general that for cross sections for direct excitations.

BENCHMARK CALCULATIONS FOR ELECTRON COLLISIONS WITH COMPLEX ATOMS

OLEG ZATSARINNY AND KLAUS BARTSCHAT

Drake University, Des Moines, Iowa, USA

The B-spline R-matrix (BSR) approach [1,2] is based on the non-perturbative close-coupling method. As such it is, *in principle*, based on an *exact expansion* of the solution of the time-independent Schrödinger equation, as an infinite sum/integral of N-electron target states coupled to the wave function of the scattering projectile. The N-electron target states, again, can *in principle* be calculated with almost arbitrary accuracy using sufficiently large configuration-interaction expansions and the correct interaction hamiltonian. *In practice*, of course, the infinite expansions have to be cut off in some way and the exact hamiltonian may not be available. In the collision part of the BSR method, the integral over the ionization continuum and the infinite sum over high-lying Rydberg states are replaced by a finite sum over square-integrable pseudo-states. Also, a number of inner shells are treated as (partially) inert, i.e., a minimum number of electrons are required in those subshells.

There are several sources of errors that need to be considered. These include but are not limited to:

1) Errors in the structure description of the target states (energy levels, oscillator strengths, polarizabilities).
2) Errors associated with the cut-off in the close-coupling expansion, including inert subshells.
3) Approximations made in the treatment of relativistic effects.
4) Numerical approximations (integration/discretization schemes, use of an R-matrix box to account for exchange and full correlation only inside the box, etc.)

Similar to experiment, it is very difficult (if not impossible) to estimate systematic errors. Regarding the above sources of error, we will make a few statements below. These statements are *most important for neutral targets*, which are also the most difficult ones to deal with when it comes to correlation effects. We also emphasize that the uncertainty generally depends on several factors, such as the quantity of interest (rate coefficient, integrated cross section, differential cross section, specific transition, energy, etc). While it is impossible to make a general statement about the uncertainties that would cover (nearly) all cases, we will summarize a few important points. It is also critical to note that these statements are based on the assumption that no currently unknown effects, which one could classify as "new physics", are sufficiently important to change the outcome to the extent that the results really matter for plasma applications. Whether or not something really "matters", of course, depends on a sensitivity check, which would have to be carried out by the data user community.

1) The BSR approach with term-dependent (and hence non-orthogonal) orbitals allows for a highly accurate target description, which *can be improved systematically,* essentially limited only by the available computational resources. Hence we generally consider the associated error in the structure

part as small compared to item 2). Also, since experimental structure data are often reliable, we can estimate the uncertainty of the collision results by analyzing the accuracy of the structure data. For example, if the theoretical oscillator strength differs from a (reliable) experimental value by 10%, it is virtually certain that the collision results at high energies are off by 10% (in the same direction) as well. Consequently, we can reduce the errors by rescaling the results with the ratio of the accepted oscillator strength and the one we obtained theoretically.

2) The cut-off in the close-coupling expansion is, most likely, *by far* the largest uncertainty in our calculations. We hence perform extensive convergence checks by varying the number and type (physical vs. pseudo) of coupled states. However, since there is *no guarantee* that the convergence rate to the correct result is steady, we have to rely on experience and generally accepted guidelines — both of which *could be wrong* and lead to unpleasant surprises. Unfortunately, experimental data often have major uncertainties as well; in some cases we compare with predictions from other large-scale calculations such as convergent close-coupling (which, however, *may* suffer from the same problems as our own).

3) We can perform non-relativistic calculations with re-coupling of the results into a relativistic scheme, semi-relativistic calculations that account for relativistic corrections at the level of first-order perturbation theory, and finally use the Dirac-Coulomb hamiltonian. Comparing the predictions, as well as using generally trusted "rules of thumb", allow for an estimate of the uncertainties.

4) We can change the range and density of the pseudo-states as well as the size of the R-matrix box. While there is, again, *no guarantee regarding potential systematic errors*, we believe that these errors are in practice negligible compared to other sources of error. *An exception may be* the fact that we cannot match to the proper three-body asymptotic condition for ionization processes. The only (and very expensive) test we can form here involves a systematic variation of the size of the R-matrix box.

Finally, it is worth pointing out that the BSR method is very general and can be used for a variety of processes, including structure calculations as well as photon- and electron-induced collisions. A list of all calculations performed until about the end of 2012 can be found in the recent Topical Review [2]. Based on experience and many comparisons with other theoretical predictions as well as experimental data, we believe that the BSR method is among the most accurate approaches available to date for electron-atom and electron-ion collisions at low and intermediate energies. It can be used to map the near-threshold resonance structure and to push the calculations up to a few times the ionization energy, where the results could likely be matched to predictions from perturbative approaches based on the distorted-wave Born approximation.

[1] O. Zatsarinny, Comp. Phys. Comm. 174 (2006) 273

[2] O. Zatsarinny and K. Bartschat, J. Phys. B 47 (2013) 112001

CONVERGENT CLOSE-COUPLING CALCULATIONS FOR ELECTRON-ATOM AND ELECTRON-MOLECULE SCATTERING

DMITRY FURSA, M. C. ZAMMIT, C. J. BOSTOCK, I. BRAY

Curtin University, Western Australia

The Convergent Close-Coupling (CCC) method developed in our group has been applied extensively to study electron-atom/ion collisions and recently has been extended to electron collisions with diatomic molecules. This approach relies on the ability to represent the infinite number of target bound states and its continuum via a finite number of states obtained by a diagonalization of the target in a square-integrable (Sturmian) one-electron basis. We normally use a Laguerre basis though other choices are possible, for example a boxed-based basis or a B-spline basis. The choice of the basis is governed by the physical problem under consideration.

As the size of a Sturmian basis increases the calculated negative energy states (relative to the corresponding ionization stage of the target) converge to the target true bound states and the positive energy states provide an increasingly dense representation of the target continuum. We then perform a multichannel expansion of the total (projectile plus target electrons) wave function and formulate a set of close-coupling equations. These equations are transformed into momentum space where they take the form of the Lippmann-Schwinger equations for the T-matrix. A solution of the T-matrix equations is obtained at each total energy E by converting them into a set of linear equations that are solved by standard techniques. We perform a partial-wave expansion of the projectile wave function and take into account the symmetry of the scattering system (e.g, total spin, parity, etc.) in order to reduce the size of the coupled equations and make calculations feasible. As soon as the T-matrix is obtained we can evaluate scattering amplitudes and cross sections for the transitions of interest.

For the case of molecular targets the formulation is done within the fixed-nuclei approximation. We adopt a single-centre approach in CCC calculations. This allows us to utilize a great deal of computational development thoroughly tested for collisions with atoms. An account of nuclear motion is done as post-processing of the fixed nuclei results that require performing fixed-nuclei calculations at a (large) number of inter-nuclei distances R.

The possible sources of errors are:

- Numerical issues related to the solution of the close-coupling equations. These types of errors can be minimized and thoroughly tested. The problem arises for very large close-coupling expansions that could lead to ill-conditioned system of linear equations. Normally we would expect an accuracy of about 3% or better.
- Accuracy of the calculated target wave functions is very important to produce accurate collision data. A structure model utilized in collision calculations has to be sufficiently accurate but at the same time it should still make collision calculations feasible. Often one has to compromise, step away from fully *ab-initio* calculations and use approximate techniques (such as phenomenological polarization potentials). Energy levels are often known to high accuracy and they can be reproduced relatively easy within the CCC approach. It is more difficult to produce correct optical oscillator strengths which are often not known from experiment with high accuracy. This is a very target dependent problem with accuracy ranging from less than 1% for hydrogen to more than 10% for complex atoms and molecules.
- Partial-wave expansion can be a source of uncertainty. This is much less an issue for collisions with atoms but it becomes a serious problem for molecular targets. For diatomics we can run calculations that account for orbital angular momentum up to L=9 of projectile electron and use a top-up procedure for larger values of L. We expect the accuracy of less than 1%.
- The size of close coupling expansion is the major source of uncertainty in close-coupling calculations. In calculations for electron scattering from atoms the size of close-coupling expansion can be very large (more than 500 states). This allows producing converged results to better than 1% accuracy for strong transitions and better than 5% for weak transitions. We expect that we will be able to achieve similar accuracy for electron collisions with diatomic

molecules. It is highly unlikely that close-coupling calculations for more complex molecules can be taken to convergence in foreseeable future and large errors (>30%) can be expected for individual transitions.
- Collisions with heavy atoms and molecules might require a fully relativistic formulation based on the Dirac equation. Failure to do this can lead to large errors (>30%) in particular for weak transitions.

How to estimate uncertainties:
- Numerical issues can be investigated by changing the accuracy of the underlying numerical methods. This is something that is routinely done and only numerically stable results would be presented and published.
- Calculations can be performed with a number of target structure models that are more or less accurate. This allows us to establish the sensitivity of the calculated collision data on the variations of the target structure.
- Partial-wave expansion can be performed with increasingly larger number of terms that allows us to estimate the convergence rate.
- Calculations with increasingly large number of target states allow us to establish the convergence rate of the close-coupling expansion.
- Relativistic effects can be an issue only if calculations are performed within the nonrelativistic approximation and then corrected for the relativistic effects. Errors in this case can be uncontrollable. It is just simpler/safer to use a fully relativistic formulation based on the Dirac equation.

UNCERTAINTIES OF MOLECULAR STRUCTURAL PARAMETERS

ATTILA G. CSÁSZÁR

Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University and MTA-ELTE Research Group on Complex Chemical Systems, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary

The most fundamental property of a molecule is its three-dimensional (3D) structure formed by its constituent atoms (see, *e.g.*, the perfectly regular hexagon associated with benzene). It is generally accepted that knowledge of the detailed structure of a molecule is a prerequisite to determine most of its other properties.

What nowadays is a seemingly simple concept, namely that molecules have a structure, was introduced into chemistry in the 19th century. Naturally, the word changed its meaning over the years. Elemental analysis, simple structural formulae, two-dimensional and then 3D structures mark the development of the concept to its modern meaning. When quantum physics and quantum chemistry emerged in the 1920s, the simple concept associating structure with a three-dimensional object seemingly gained a firm support. Nevertheless, what seems self-explanatory today is in fact not so straightforward to justify within quantum mechanics. In quantum chemistry the concept of an equilibrium structure of a molecule is tied to the Born-Oppenheimer approximation but beyond the adiabatic separation of the motions of the nuclei and the electrons the meaning of a structure is still slightly obscured. [1]

Putting the conceptual difficulties aside, there are several experimental, empirical, and theoretical techniques to determine structures of molecules. One particular problem, strongly related to the question of uncertainties of “measured” or “computed” structural parameters, is that all the different techniques correspond to different structure definitions and thus yield different structural parameters. Experiments probing the structure of molecules rely on a number of structure definitions, to name just a few: r_0, r_g, r_a, r_s, r_m, etc., and one should also consider the temperature dependence of most of these structural parameters which differ from each other in the way the rovibrational motions of the molecules are treated and how the averaging is performed. Simply, there are significant disagreements between the same bond lengths measured by different techniques. These disagreements are, however, systematic and can be computed via techniques of quantum chemistry which deal not only with the motions of the electrons (electronic structure theory) but also with the often large amplitude motions of the nuclei.

As to the relevant quantum chemical computations, since about 1970 electronic structure theory has become able to make quantitative predictions and thus challenge (or even overrule) many experiments. Nevertheless, quantitative agreement of quantum chemical results with experiment can only be expected when the motions of the atoms are also considered. In the fourth age of quantum chemistry [2] we are living in an era where one can bridge quantitatively the gap between 'effective', experimental and 'equilibrium', computed structures at even elevated temperatures of interest thus minimizing any real uncertainties of structural parameters.[3]

The connections mentioned are extremely important as they help to understand the true uncertainty of measured structural parameters. Traditionally it is microwave (MW) and millimeterwave (MMW) spectroscopy, as well as gas-phase electron diffraction (GED), which yielded the most accurate structural parameters of molecules. The accuracy of the MW and GED experiments approached about 0.001Å and 0.1° under ideal circumstances, worse, sometimes considerably worse, in less than ideal and much more often encountered situations.

Quantum chemistry can define both highly accurate equilibrium (so-called Born-Oppenheimer, r_e^{BO}, and semiexperimental, r_e^{SE}) structures and, via detailed investigation of molecular motions, accurate temperature-dependent rovibrationally averaged structures. Determining structures is still a rich field for research,[4] understanding the measured or computed uncertainties of structures and structural parameters is still a challenge but there are firm and well-established guidelines. At present it seems that the best structures, both the most accurate ones and the ones easiest to compare when structural trends are sought, are the semiexperimental equilibrium structures. The r_e^{SE} structures are based on semiexperimental equilibrium rotational constants, B_e^{SE}, which are the corrected effective rotational constants B_0 "measured" for a given isotopologue and are corrected for the rovibrational effect using a computed cubic force field. The r_e^{SE} structure of the molecule is determined via a least-squares fit of the structural parameters to the B_e^{SE}s. During the large number of such structural studies, some on molecules as large and complex as amino acids, including glycine,[5] alanine,[6] and proline,[7] it became clear that the "measured" rotational constants are often not accurate enough for the purposes of accurate structure determination and they need to be refitted using the method of predicate observations.[4,8] The method of predicate observations can also be used during the structural fitting and yields more reliable and tighter uncertainties for the refined structural parameters. With the joint clever use of experiment and theory one can routinely achieve the 0.001 Å and 0.1° accuracy which previously could characterize only the most elaborate experiments.

[1] Mátyus E, Hutter J, Müller-Herold U, Reiher M. J. Chem. Phys. 2011, 135, 204302.
[2] Császár AG, Fábri C, Szidarovszky T, Mátyus E, Furtenbacher T, Czakó G. Phys. Chem. Chem. Phys. 2012, 14, 1085.
[3] Czakó G, Mátyus E, Császár AG. J. Phys. Chem. A 2009, 113, 11665.
[4] Demaison J, Boggs JE, Császár AG. (eds.) Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry, CRC Press: Boca Raton, 2011
[5] Kasalová V, Allen WD, Schaefer HF, Czinki E, Császár AG. J. Comp. Chem. 2007, 28, 1373.
[6] Jaeger HM, Schaefer HF, Demaison J, Császár AG, Allen WD. J. Chem. Theory Comput. 2010, 6, 3066.
[7] Allen WD, Czinki E, Császár AG. Chem. Eur. J. 2004, 10, 4512.
[8] Bartell LS, Romanesko DJ, Wong TC. Augmented Analyses: Method of Predicate Observations, in Chemical Society Specialist Periodical Report No. 20, Chem. Soc.: London, 1975.

CALCULATION OF DISSOCIATIVE ELECTRON ATTACHMENT CROSS SECTIONS

DANIEL J HAXTON

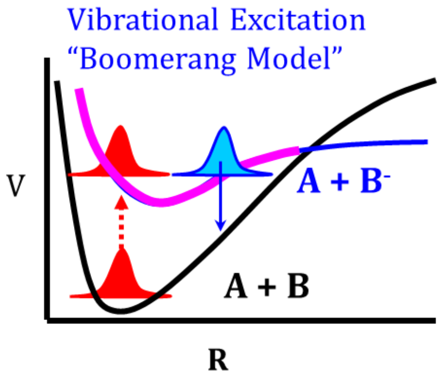
Atomic, Molecular, and Optical theory group, Lawrence Berkeley National Lab, CA, USA

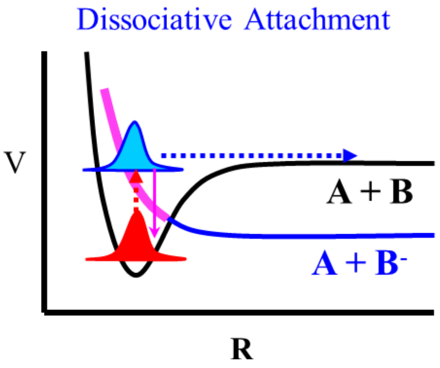
Dissociative electron attachment (DEA) is the process simply written $AB + e^- \rightarrow AB^- \rightarrow A^- + B$.

However, it may also involve e.g. three-body breakup. DEA may be difficult to calculate due to strong competition between dissociation ($AB^- \rightarrow A^- + B$) and autoionization ($AB^- \rightarrow AB + e^-$).

We describe the process using the standard Born-Oppenheimer picture with electronic states having energies as a function of nuclear geometry. As the internuclear geometry is varied, there may be bound anion electronic states that become unbound or vice-versa, i.e., there may be internuclear geometries at which the electron affinity crosses the value zero.

An electron with the proper kinetic energy can attach to make a wave packet on a metastable state potential energy surface. The shorter-lived the state is, the more likely it is that the electron will detach (the inverse process), in which case the net result of the scattering event is rovibrational excitation (left figure). However, if the state is long-lived enough, the molecule may distort and reach geometries at which the anion state becomes bound (right figure). Autoionization is then impossible, and if the system continues to dissociation, dissociative electron attachment has occurred.





For the purpose of exposition the DEA cross section may be parameterized simply as $\sigma_{DEA} \sim \Gamma e^{-\Gamma t_{diss}}$

Here the quantity Γ is the width of the state, proportional to the attachment probability and inversely proportional to the lifetime; the time t_{diss} is that taken to reach the bound region. So, a very narrow (small width, long lived) resonance has a low attachment probability, but once the electron is attached it is almost guaranteed to survive to dissociation, in which case calculating the process is very similar to calculating photodissociation. In contrast, a short lived electronic state will suffer from a small survival probability, and the specifics of both the energy and lifetime of the resonance, as functions of internuclear geometry, may be largely responsible for producing the observed final states. In this case, estimating even the correct order of magnitude may require explicit calculations of the dissociation on a multidimensional, complex-valued potential energy surface.

These issues will be discussed with particular emphasis on electrons incident on H_2O, CO_2 and NO.

CALCULATIONS OF ELECTRON-MOLECULE SCATTERING CROSS SECTIONS USING THE R-MATRIX METHOD

JIMENA D. GORFINKIEL

Department of Physical Sciences, The Open University, Milton Keynes, UK

Method:

The R-matrix method (as implemented in the UKRmol suite) is used to solve the electronic part of the electron-molecule scattering problem below the ionization threshold of the target (calculations above the ionization threshold including pseudostates have been performed for 2 electron systems but are less accurate). The method is based in the separation of space into an inner region and an outer region. In the inner region scattering and target electrons are indistinguishable and the method uses sophisticated computational chemistry techniques to determine the wavefunctions that describe the target + scattering electron system. In the outer region exchange and correlation can be neglected and a multipolar expansion of the interacting potential suffices to describe the collisions. The method only allows for the explicit inclusion of a few partial waves in the calculation. When the target has a permanent dipole moment, it is necessary to determine the contribution of the higher partial waves using a less computationally demanding approach. On our case, we use an approach based on the Born approximation that incorporates the rotational motion and therefore overcomes the divergence of the fixed-nuclei cross sections.

The method is more intensively used to determine electronically elastic and inelastic integral cross sections, electronically elastic differential cross sections and resonance parameters (position and width) for both small and medium-sized molecular targets. Its output is also used to determine rotational and vibrational excitation cross sections, as well as to perform calculations for dissociative recombination, dissociative electron attachment, etc.

Sources of uncertainty:

The input required for an R-matrix calculation can be roughly divided in two types: data that is used to generate wave functions (basis set, choice of configurations if a configuration interaction approach is used) and data that is used directly (molecular geometry, permanent and transition moments for all electronic states included in the calculation, excitation thresholds, etc.). (It should be noted, however, that it is usual in R-matrix calculations to use excitation thresholds and permanent/transition moments that are consistent with the target wavefunctions used in the inner region, even if they are known to be poor). Other parameters (number of partial waves included in the ab initio calculation, quality of the description of the discretized continuum in the inner region) are regularly tested to ensure 'convergence'.

Leaving aside the uncertainties associated with both the approximations used (Born-Oppenheimer, Fixed-Nuclei, etc.) and those linked to the numerical procedures employed, the quality of the cross sections depends strongly on the number of electronic states included in the calculation and the quality of the wave function describing these (the resonance parameters also depend strongly on the quality of the description of the polarization effects). The uncertainty in the wavefunctions (target and target+ scattering electron) is hard to ascertain. One could look at using a range of basis sets to study a specific target in order tto estimate how much some calculated quantity (energy, permanent dipole and/or quadrupole moment) changes with basis set, but this may not have a direct link to the precision of the cross sections.

For the data that is used directly it should be possible to relate the uncertainty in the cross section to the uncertainty in these quantities. In this case, a well selected set of benchmark systems (e.g. dipolar and non-dipolar targets) should perhaps provide an estimate for a larger set of molecules.

Uncertainty Quantification

It is routine in R-matrix studies to perform calculations for a variety of models in order to assess which is the most appropriate. These results (provided the models are chosen carefully) could provide an estimate of uncertainties for each calculation performed. It is also customary to test 'convergence' with a number of parameters (number of partial waves, R-matrix radius). Again these tests (performed for some benchmark systems, perhaps) should allow us to estimate uncertainties linked to these parameters for other targets.

Comparison of results calculated with different methods could be another way of looking at the precision of our results. One could start by choosing a model that two or more methods can use to perform (what should be) identical calculations. Any discrepancies in this case would be linked to limitations of the computational implementation of the method. One could then study a few benchmark systems using the models that are regularly employed to perform calculations with each method. This study would give us an idea of the uncertainty linked to employing a specific method.

UNCERTAINTY IN MOLECULAR PHOTOIONIZATION

ROBERT R. LUCCHESE

Department of Chemistry, Texas A&M University, USA

Theoretical Method Description

The theoretical methods for computing electron-molecule collision which I will discuss are based on single-center expansions.[1,2] The structure of the wave function is a traditional close-coupling expansion. The total wave function is written as

$$\Psi_S = \sum_i A\left(\Phi_i, \chi_{S,i}\right) \tag{1}$$

where $\chi_{S,i}$ is the one-electron continuum function with asymptotic state S for the target state Φ_i that is written as a linear combination of configuration state functions (CSFs), ψ_j,

$$\Phi_i = \sum_j c_{ij}\psi_j \tag{2}$$

In a typical project,[3] the expansion in equation (2) includes up to ~ 10,000 CSFs

A wide class of observables, M, can be computed with such wave functions by computing matrix elements of the form

$$M = \langle R|\Psi_s\rangle. \tag{3}$$

This includes dipole transition matrix elements for photoionization as well as the scattering matrix. The scattering state Ψ_S is a solution of the Lippmann-Schwinger equation

$$|\Psi_S\rangle = |\mathrm{S}\rangle + G_0\mathrm{V}|\Psi_S\rangle. \tag{4}$$

Additionally, there is a conjugate equation

$$\langle\Theta_R|(1 - G_0\mathrm{V}) = \langle R. \tag{5}$$

The matrix elements of the form given in equation (3) can then be computed employing the Schwinger variational expression[4] where Ψ_S and Θ_R expanded in basis sets $\{u_i\}$ and $\{v_i\}$, respectively, leading to the expression

$$M = \sum_{i,j} \langle R|u_i\rangle \, D_{ij}^{-1} \langle v_j|S\rangle \tag{6}$$

where

$$D_{ij} = \langle v_i (1 - G_o V)|u_j\rangle. \tag{7}$$

To compute the matrix elements required to evaluate equations (6) and (7) we expand all functions about a single center using the form

$$\langle \vec{r}|f\rangle = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} f_{lm}(r) Y_{lm}(\hat{r}). \tag{8}$$

For small molecules, this expansion can be well converged using, for example, $l_{\max} = 50$ for CO[3] and $l_{\max} = 80$ for N_2O[5].

The approach outlined here has been implemented for linear molecules in its most general form.[1,2] For larger, non-linear systems a simplified static-exchange model has been implemented,[6-8] where Φ_i is represented by a single CSF and only one channel is retained in equation (1).

Quantities of interest (QOI) in molecular photoionization include the total cross section, photoelectron asymmetry parameter, the position of resonances and widths, and molecular frame angular distributions, which can all be computed using matrix elements of the form given in equation (3).

Sources of Uncertainties

There are three categories of uncertainties in the computed QOI.

Uncertainties due to the physical model

First is the treatment of the vibrational motion in molecular systems. The most common approximation is to just use the fixed nuclei approximation. If the process is very sensitive to geometry, then the next level of approximation would be the adiabatic nuclei or Chase approximation.[9] In this approach, the electron scattering calculations are still performed in the fixed nuclei approximation, but the final observable is computed be performing the appropriate integral of the geometry dependent transition matrix elements multiplied by vibrational wave functions. Going beyond the adiabatic approximation may be important where there are avoided corssings or, more generally, conical intersections.

Uncertainties due to truncations in the N-electron wave function expansions

The second source of error is the truncation of the close-coupling expansion given in equation (1). For most applications in molecular systems it is difficult to convergence this expansion. A related source of error is the truncation of the configuration interaction expansion of the target states given in equation (2). Additionally, the potential V in equation (4) usually comes from the non-relativistic Schrodinger equation, so to the extent that relativistic effects are significant either the potential must be modified, or this becomes a source of error.

Uncertainties due to truncations in the one-electron wave function expansions

The third source of errors are the numerical approximations introduced in the evaluation of the matrix elements of equations (6) and (7). These errors are controlled by the density of the radial and angular grids used to compute the matrix elements and the value of $l_{\max}$ used to truncate the single-center expansion given in equation (8). Additionally, the one-electron basis set used to expand the orbitals can also be a source of error in the representation of the orbitals used in the target orbital expansions. Note that limitations in the one-electron basis set can also lead to errors in the N-electron wave function if the expansion in CSFs given in equation (2) depends on the size of the one-electron basis set, as would be the case, for example, in a multi-reference singles and doubles configuration interaction type wave function.

How to Estimate Uncertainties

I will consider the possibilities for estimating errors in the reverse order from how the sources of errors were presented above. Within a certain model and level of calculation, with a given choice for the Hamiltonian and *N*-electron expansion, uncertainties resulting from the choice of radial and angular grids can be assessed by employing numerical self-convergence for a given QOI. The convergence with respect to increasing one-electron basis set size can by estimated using the standard tools of quantum chemistry such as the complete basis-set extrapolation.[10]

Assessing the uncertainty due to the limitations of the *N*-electron expansion involves studying the convergence of a computed QOI with respect to the levels of correlation, i.e. channel expansion. For example, in molecular photoionization calculations one could consider models employing the single-channel approximation, coupled channel calculations, and different levels of correlation in the description target wave functions. It is difficult to actually converge such expansions, however one should at least compute the QOI with the most correlated wave function and compare that to a calculation with less correlation. This can provide a rough estimate of the size of the uncertainties.

The effects of vibrational motion are also difficult to assess in larger systems due to the large number of vibrational modes available in such systems. It may be possible to consider the individual effects of single modes, or two coupled modes, or more generally of an *N*-mode expansion.[11] However, solving the vibrational problem becomes exponentially difficult with respect to the number of atoms, so that a full treatment quickly become unfeasible.

Additionally, in photoionization there is a consistency test that compares different forms of the theory which should yield the same results, e.g. a comparison of cross sections computed in the length and velocity forms.

At the current time, the computation of most QOI for electron collisions in molecular systems beyond H_2 or H_3^+, can at best provide [12] “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.”

References

[1] R. E. Stratmann and R. R. Lucchese, J. Chem. Phys. 102, 8493 (1995).

[2] R. E. Stratmann, R. W. Zurales, and R. R. Lucchese, J. Chem. Phys. 104, 8989 (1996).

[3] M. Lebech, J. C. Houver, G. Raseev, A. S. Dos Santos, D. Dowek, and R. R. Lucchese, J. Chem. Phys. 136, 094303 (2012).

[4] R. R. Lucchese, K. Takatsuka, and V. McKoy, Phys. Rep. 131, 147 (1986).

[5] M. Lebech, J. C. Houver, D. Dowek, and R. R. Lucchese, J. Chem. Phys. 120, 8226 (2004).

[6] F. A. Gianturco, R. R. Lucchese, and N. Sanna, J. Chem. Phys. 100, 6464 (1994).

[7] A. P. P. Natalense and R. R. Lucchese, J. Chem. Phys. 111, 5344 (1999).

[8] R. R. Lucchese, N. Sanna, A. P. P. Natalense, and F. A. Gianturco, ePolyScat: A general purpose electron-molecule scattering program (2012) http://www.chem.tamu.edu/rgroup/lucchese/ePolyScat.E3.manual/manual.html.

[9] D. M. Chase, Phys. Rev. 104, 838 (1956).

[10] T. H. Dunning, J. Phys. Chem. A 104, 9062 (2000).

[11] S. Carter, S. J. Culik, and J. M. Bowman, J. Chem. Phys. 107, 10458 (1997).

[12] Editors, Phys. Rev. A 83, 040001 (2011).

UNCERTAINTIES IN CALCULATIONS OF LOW-ENERGY RESONANT ELECTRON COLLISIONS WITH DIATOMIC MOLECULES

KAREL HOUFEK

Institute of Theoretical Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech

Processes which take place during resonant electron-molecule collisions at low energies (usually less than 10 eV) and which proceed via a temporary resonant state of negative molecular ion are especially vibrational excitation and dissociative attachment. A lifetime of the resonant electronic state is often comparable with the vibrational period of the molecule and thus the nuclear motion has to be taken into account.

Theoretical description of the dynamics of the molecular motion usually comprises two steps. First, quantum-chemical calculations of potential energy surfaces where molecular species are bound are performed using nowadays well established packages of codes and also fixed-nuclei electron scattering calculations (using e.g. UK R-matrix codes [Eur. Phys. J D 66 (2012) 58]) provide information about complex part of the potential energy surfaces (resonance positions and widths). The second step involves calculation of the vibrational dynamics on these potential energy surfaces within an appropriate approximation.

The main reason for difficulties of estimating errors is that calculations of the cross sections and rate constants of the above processes consists of several steps and although we often claim that we perform "ab initio" calculations some of these steps are not truly "ab initio", especially the determination of a complex part of the potential for nuclear dynamics and thus also the construction of the model for the nuclear dynamics. Let us discuss the most important steps in details.

There are several methods and program packages of quantum chemistry codes to calculate quite accurately (at least for systems with a few atoms) potential energy surfaces (PES) of the neutral molecule and negative molecular ion where they are bound. The error of these calculations can be often estimated from performing calculations with larger basis and perturbation corrections.

To get the complex part of the potential, i.e. the resonance positions and widths for various geometries of the molecular anion (N+1 electrons system), we usually perform fixed-nuclei electron-molecule scattering calculations based on particular expansion of N+1 electronic wave function (SE, SEP, CAS etc) where we can change some of the parameters (e.g. the number of virtual orbitals or the number of target states) to avoid under- or over- correlation of N+1 electron system. But to be able to "adjust" properly the calculations we have to know in advance where the resonance is. And these "ad hoc" adjustments lead to main difficulties for uncertainty estimates of the entire theoretical calculation which must be then based on the knowledge of errors e.g. in the experimental determination of resonance position. Therefore we suggest that the electron scattering calculations should be adjusted in such a way that they would closely reproduce the PES of the molecular anion where it is bound. Then we can estimate the error of the complex part of the PES from comparison of several such scattering models.

Finally, there are several models which treat the nuclear dynamics at different levels of approximation, e.g. effective range, local complex potential (LCP) approximation, nonlocal resonance model (NRM) etc. If we perform calculation within a chosen approximation it is often quite difficult to estimate the error of the method if we do not try to construct a better model. Then only by comparison with experiment one can estimate the accuracy of the calculation. One possibility (independent of experiment) of how to estimate accuracy of a given approximation to nuclear dynamics (at least for diatomic molecules) is to use a two-dimensional model of electron-molecular collisions [Phys. Rev. A 73 (2006) 032721; Phys. Rev. A 77 (2008) 012710] which can be solved both numerically exactly and within various approximations so we can estimate the uncertainty from such model calculations. It was shown for several systems that the error in the cross sections depends (sometimes dramatically) on both the energy of an incoming electron and on the initial and final vibrational state of the molecule and it is in general larger for LCP approximation than for NRM. Furthermore, all practically used approximations for nuclear dynamics provide only resonant contribution to the cross sections, but for the vibrational excitation and especially for elastic cross sections there can be significant "background" contribution which is not usually taken into account.

LOW-ENERGY ELECTRON SCATTERING DATA FOR CHEMICAL PLASMA TREATMENT OF BIOMASS

MARCO A. P. LIMA

Departamento de Eletrônica Quântica, Instituto de Física da Unicamp, Brazil

Replacing fossil fuels with biofuels from renewable sources is an important goal for reducing greenhouse gas emissions. Many countries are already using few percent of ethanol in the gasoline and few of them, with more aggressive programs, have developed flex fuel engines that can run with any mixture of gasoline and ethanol. An important point is how to produce ethanol in a sustainable way and with which technology? Biomass is a good candidate since it has cellulose and hemicellulose as source of sugars. In order to liberate these sugars for fermentation, it is important to learn how to separate the main components. Chemical routes (acid treatment) and biological routes (enzymatic hydrolysis) are combined and used for these purposes. Atmospheric plasmas can be useful for attacking the biomass in a controlled manner and low-energy electrons may have an important role in the process. Recently we have been studying the interaction of electrons with lignin subunits (phenol, guaiacol, p-coumaryl alcohol), cellulose components, β-D-glucose and cellobiose (β(1 - 4) linked glucose dimer) and hemicellulose components (β-D-xylose). We also obtained results for the amylose subunits α-D-glucose and maltose (α(1 - 4) linked glucose dimer). Altogether, the resonance spectra of lignin, cellulose and hemicellulose components establish a physical–chemical basis for electron-induced biomass pretreatment that could be applied to biofuel production. In my talk I will give a progress report on this matter. We will also discuss microsolvation effects on the electron-phenol scattering process and present our strategy to study molecular dissociation through electronic excitation of low energy triplet states.

EVALUATION PROCEDURES OF RANDOM UNCERTAINTIES IN THEORETICAL CALCULATIONS OF CROSS SECTIONS AND RATE COEFFICIENTS

V. KOKOOULINE AND W. RICHARDSON

Department of Physics, University of Central Florida, Orlando, FL, USA

Uncertainties in theoretical calculations may include:

- Systematic uncertainty: Due to applicability limits of the chosen model.
- Random: Within a model, uncertainties of model parameters result in uncertainties of final results (such as cross sections).
- If uncertainties of experimental and theoretical data are known, for the purpose of data evaluation (to produce recommended data), one should combine two data sets to produce the best guess data with the smallest possible uncertainty.

1. Evaluation of uncertainties within a chosen model

If there are not that many parameters, one can simply vary them within a reasonable interval and see the effect of the variation on the final results (cross sections). It is a sort of sensitivity test. There are two systematic approaches: Least squares methods and Monte-Carlo methods

Least-squares method

Given two sets of data with uncertainties on the same grid of energies (E_i, i=1,2,..), the best guess (evaluated) cross section σ_i^{rec} is obtained by minimizing the following function

$$F = \sum \left(\frac{\left(\sigma_i^{rec} - \sigma_i^{\exp}\right)^2}{\Delta\sigma_i^{\exp}} + \frac{\left(\sigma_i^{rec} - \sigma_i^{the}\right)^2}{\Delta\sigma_i^{the}} \right).$$

Uncertainty $\Delta\sigma_i^{\mathrm{rec}}$ of evaluated (recommended) data is not available but can be obtained in a statistical analysis. The approach is good if results (σ_i^{the} or σ_i^{exp}), obtained for different energy points data points, are not correlated. Usually, theoretical results are strongly correlated: changing a parameter in the theoretical model changes cross sections for all energy points E_i. Experimental cross sections measured at different E_i may also be correlated.

Covariance matrix and variance

The mean value, for example, calculating (measuring) σ at energy E_i is,

$$\langle \sigma_i \rangle = \int \sigma_i P(\sigma_i) d\sigma_i \,.$$

In theoretical calculations, some of theoretical parameters p_j are described by similar formulas. For example, if a potential energy surface on j=1,..,N_{pes} grid point is used, it introduces N_{pes} parameters p_j, each having it own uncertainty.

Strictly speaking, one has to calculate an N-dimensional integral if there are several variables:

$$\langle p_j \rangle = \int p_j P(p_{1,} p_{2,} \cdots, p_j, \cdots) d\vec{p} \qquad \langle \sigma_i \rangle = \int \sigma_i P(\sigma_{1,} \sigma_{2,} \cdots, \sigma_i, \cdots) d\sigma$$

Uncertainty (standard deviation) is $\Delta\sigma_i = \sqrt{\left\langle \left(\sigma_i - \langle \sigma_i \rangle\right)^2 \right\rangle} = \sqrt{\langle \sigma_i^2 \rangle - \langle \sigma_i \rangle^2}$.

Covariance matrix describes correlation between variables:

$$V_{ii'} = \left\langle \left(\sigma_i - \langle \sigma_i \rangle\right)\left(\sigma_{i'} - \langle \sigma_{i'} \rangle\right) \right\rangle = \langle \sigma_i \sigma_{i'} \rangle - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle \,.$$

It shows how a change in a parameter of a given theoretical model (or even in an experiment) changes cross sections at all energy points.

When $i=i'$: $V_{ii} = (\Delta\sigma_i)^2$, which is variance.

If experimental and theoretical covariance matrices V^{exp} and V^{the} are known, then one has to minimize F

$$F = (\vec{\sigma}^{rec} - \vec{\sigma}^{exp}) V_{exp}^{-1} (\vec{\sigma}^{rec} - \vec{\sigma}^{exp}) + \left(\vec{\sigma}^{rec} - \vec{\sigma}^{the}\right) V_{the}^{-1} \left(\vec{\sigma}^{rec} - \vec{\sigma}^{the}\right),$$

written as a matrix product here with cross sections represented in a vector form

$$\vec{\sigma}^{rec} = (\sigma_1^{rec}, \sigma_2^{rec}, \dots), \vec{\sigma}^{the} = \left(\sigma_1^{the}, \sigma_2^{the}, \dots\right), \vec{\sigma}^{exp} = \left(\sigma_1^{exp}, \sigma_2^{exp}, \dots\right).$$

If there are several parameters in the theoretical model, finding the minimum of F is difficult. Covariance matrix or/and uncertainties of the evaluated data are not available immediately.

A better way to determine the evaluated cross section is the Bayesian statistics approach.

Bayesian statistics methods

An alternative to the least-squared method is to apply a Monte-Carlo/Bayesian approach. We used a modified UMC approach by Capote *et al.* Monte-Carlo approaches account for the uncertainty propagation in theoretical calculations in a systematic way. The method combines theoretical and experimental data (generally, data from two independent sources) and produces evaluated data. The two data sources should have uncertainties or covariance matrices. The “evaluation” procedure is based on the Bayesian statistics.

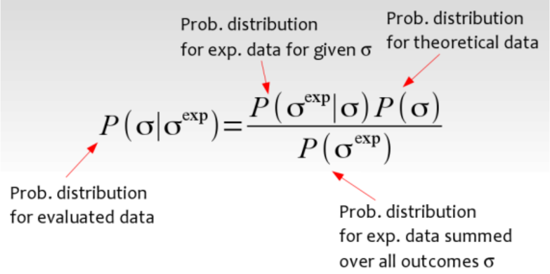
Bayes formula gives the probability $P(W|L)$ of an event W at the condition that event L was observed. If $P(L)$, $P(W)$, and $P(L|W)$ are given then

$$P(W\,|\,L)=\frac{P(L\,|\,W)P(W)}{P(L)}$$

For data evaluation: Consider cross section σ at energy E. A theoretical model and uncertainties of its parameters produce an uncertainty in σ (by the means of uncertainty propagation) and the corresponding probability distribution $P(\sigma)$.

If experimental data is considered as additional data (information “L”), one can use Bayes' formula to calculate probability $P(W|L)$ that the “actual” cross section has value σ.

This approach combines data and uncertainties from two sources.



Bayes' theorem for combined theoretical & experimental data

Main formulas

$$P(\sigma) = N_{the}\exp\left\{-\frac{1}{2}\left[(\vec{\sigma}-\vec{\sigma}^{the})(\hat{V}^{the})^{-1}(\vec{\sigma}-\vec{\sigma}^{the})\right]\right\}$$

$$P(\sigma^{exp}|\sigma) = N_{exp}\exp\left\{-\frac{1}{2}\left[(\vec{\sigma}-\vec{\sigma}^{exp})(\hat{V}^{exp})^{-1}(\vec{\sigma}-\vec{\sigma}^{exp})\right]\right\}$$

$$P(\sigma^{\exp})=\int d\sigma P(\sigma^{\exp}\,|\,\sigma)P(\sigma)$$

N_{the} and N_{exp} are normalization constants, but they are canceled out and need not to be calculated. Using simpler notations:

$$P(\sigma\,|\,\sigma^{\exp})\rightarrow P_{rec}(\sigma)=\frac{P_{\exp}(\sigma)P_{the}(\sigma)}{\int P_{\exp}(\sigma)P_{the}(\sigma)d\sigma}.$$

Procedure of determination of theoretical uncertainties and evaluated cross sections

(a) Choice of the energy grid, E_i (i=1,...,N): For evaluation, the grid should be the same as in experiment.

(b) Varying parameters within an interval of a few Δp_j, and calculating σ_i^k for each set k of parameters. Then averaging over p (summation over k) is performed: mean values $<\sigma_i>$ and covariance matrix are obtained

$$\langle \sigma_i \rangle = \int \sigma_i P(p_{1,} p_{2,} \cdots, p_j, \cdots) d\vec{p}$$

$$V_{ii'}^{the} = \langle \sigma_i \sigma_{i'} \rangle - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle = \int \sigma_i \sigma_{i'} P(p_{1,} p_{2,} \cdots, p_j, \cdots) d\vec{p} - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle$$

One can evaluate above multidimensional integrals on a uniform grid or use the Gaussian quadrature. It is slow if the model has many parameters.

(c) One can use a Monte-Carlo approach for the integration. For this purpose, one chooses randomly a set k of parameters p_j^k, such that p_j^k is within the interval $<p_j>\pm\psi\Delta p_j$, with ψ~4-6, i.e.

$$p_j^k = \langle p_j \rangle + (2\gamma - 1)\psi \Delta p_j \,,$$

where γ is a random number between 0 and 1. Then, the mean value and covariance matrix are

$$\langle \sigma_i^{the} \rangle = \frac{\sum_k \sigma_i P(p_1^k, p_2^k, \cdots, p_j^k, \cdots)}{\sum_k P(p_1^k, p_2^k, \cdots, p_j^k, \cdots)} \,,$$

$$\langle \sigma_i^{the} \sigma_{i'}^{the} \rangle = \frac{\sum_k \sigma_i \sigma_{ii'} P(p_1^k, p_2^k, \cdots, p_j^k, \cdots)}{\sum_k P(p_1^k, p_2^k, \cdots, p_j^k, \cdots)} \,,$$

$$V_{ii'}^{the} = \langle \sigma_i^{the} \sigma_{i'}^{the} \rangle - \langle \sigma_i^{the} \rangle \langle \sigma_{i'}^{the} \rangle .$$

Taking into account experimental data

Experimental data and uncertainties are needed. The most likely, the covariance matrix V_{exp} is unknown. Uncertainties should be used to construct diagonal V_{exp} .

One should use a Monte-Carlo approach again because number of variables (σ_i) are now determined by the number of grid points. Now $\sigma_i^k = \langle \sigma_i \rangle + (2\gamma - 1)\psi \sqrt{V_{ii'}^{the}}$ i.e. σ_i is in the interval $<\sigma_i>\pm\gamma\Delta\sigma_i$.

Then, the mean value and covariance matrix are

$$\langle \sigma_i^{rec} \rangle = \frac{\sum_k \sigma_i P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}{\sum_k P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}, \qquad V_{ii'}^{rec} = \langle \sigma_i^{rec} \sigma_{i'}^{rec} \rangle - \langle \sigma_i^{rec} \rangle \langle \sigma_{i'}^{rec} \rangle$$

$$\langle \sigma_i^{rec} \sigma_{i'}^{rec} \rangle = \frac{\sum_k \sigma_i \sigma_{i'} P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}{\sum_k P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})},$$

$$P_{the}(\vec{\sigma}) = \exp\left\{-\frac{1}{2}\left[(\vec{\sigma} - \vec{\sigma}^{the})(\hat{V}^{the})^{-1}(\vec{\sigma} - \vec{\sigma}^{the})\right]\right\},$$

$$P_{exp}(\vec{\sigma}) = \exp\left\{-\frac{1}{2}\left[(\vec{\sigma} - \vec{\sigma}^{exp})(\hat{V}^{exp})^{-1}(\vec{\sigma} - \vec{\sigma}^{exp})\right]\right\}.$$

Conclusions

- In many situations, it is possible to assess the accuracy of theoretical calculations because theoretical models usually rely on parameters that are uncertain, but not completely random, i.e. the uncertainties of the parameters of the models are approximately known. If there are one or several such parameters with corresponding uncertainties, even if some or all parameters are correlated, the above approach gives a conceptually simple way to calculate uncertainties of final cross sections (uncertainty propagation). Numerically, the statistical approach to the uncertainty propagation could be computationally expensive. However, in situations, where uncertainties are considered to be as important as the actual cross sections (for data validation or benchmark calculations, for example), such a numerical effort is justified.

- Having data from different sources (say, from theory and experiment), a systematic statistical approach allows one to compare the data and produce "unbiased" evaluated data with improved uncertainties, if uncertainties of initial data from different sources are available.

- Without uncertainties, the data evaluation/validation becomes impossible. This is the reason why theoreticians should assess the accuracy of their calculations in one way or another. A statistical and systematic approach, similar to the described above, is preferable.

STATUS OF A&M DATABASE AND DATA ANALYSIS FOR FUSION EDGE PLASMA TRANSPORT STUDIES

DETLEV REITER

Forschungszentrum Jülich GmbH, IEF-4, 52428 Jülich, Germany

Atomic and molecular data are of relevance in fusion boundary layer plasmas, because reactive processes actively influence (and even control) the plasma flow and divertor dynamics in the near target surface domain in reactors.

These data are an important ingredient in fusion transport simulations of advective-diffusive-reaction type (codes such as B2-EIRENE (SOLPS) in EU, UEDGE in the US or SONIC in Japan). Data at the most detailed level enter such transport simulations in kinetic (microscopic) model components, i.e. neutrals (atoms and molecules, molecular ions, and weakly ionized impurity ions such as e.g. W, N, C, Be, He), whereas the macroscopic (fluid) components use condensed, reduced information and atomic collision processes.

The database HYDKIN (www.hydkin.de) of the EIRENE Monte Carlo code has been set up and is currently being developed to publicly expose the unprocessed raw A&M data used in B2-EIRENE. The underlying A&M dataset has either been compiled at FZJ in the past (e.g. the current hydrocarbon, and silane cross section databases), or data have been taken from publicly available other datasets (e.g. ADAS) or CR codes (H, H_2, He) from NIFS.

The second purpose of the online tool HYDKIN is processing and analyzing data, prior to their activation in complex transport models. 1D (either time or, recently, also 1 spatial coordinate) test cases are solved, based upon an eigenvalue analysis of the underlying reaction master matrix. This enables a forward sensitivity analysis (evaluation of sensitivity coefficients defined as logarithmic derivative of CR population density wrt. reaction rate coefficients.

The eigenvalue analysis carried out on plasma chemistry models in HYDKIN gives direct indications about the existence of underlying reduced chemistry models (e.g. by a separation of fast against slow modes). A targeted application here was a $H/H_2/H_2^+$ CR model, because presence of vibrational excitation at least of ground state H_2 (and isotopomeres) provides a rather continuous spectrum of time scales, strictly ruling out condensation of vibrational kinetics into bundled rates.

Recent extensions of HYDKIN datasets have started with respect to the Be, BeH, BeH^+ system, and the N, N^+, N_2, N_2^+ N_2- system, the former because of its relevance due to the choice of Be as ITER (and JET) main chamber material, the latter because of its possible important role as active edge plasma cooler in case of all metal divertors. Whereas the database wrt. the Be-family is rather sparse, the issue wrt. N,N_2, and their ions is just opposite: the huge amount of data available (e.g. from atmospheric research, space vehicle re-entrance issues, etc., requires primarily a critical evaluation, condensation and recommendation for the fusion community.

DATA QUALITY AND NEEDS FOR COLLISIONAL-RADIATIVE MODELING

YURI RALCHENKO

National Institute of Standards and Technology, Gaithersburg, MD, USA

Collisional-radiative (CR) calculations typically require large sets of atomic data. To this end, completeness and consistency take priority over quality although the latter can never be ignored. Moreover, high-accuracy collisional parameters, such as cross sections, are needed to set up benchmarks for CR datasets. Since CR models are generally problem-tailored, some parameters may be of no importance for one task but crucial for another. For instance, cross section values become less and less important for high densities where LTE limit is approached.

New problems in plasma spectroscopy call for new datasets that have never been important before. The recent examples include scattering amplitudes and off-diagonal density matrix elements for proton-hydrogen scattering (important in the motional Stark effect diagnostics) and m-resolved cross sections of dielectronic capture for analysis of anisotropic dielectronic resonances in EBIT measurements.

Monte Carlo simulations of error propagation in CR models are a powerful and universal technique. We performed such tests (~1,000,000 runs) for the analysis of moments in steady-state ionization/recombination of Ne and C plasmas. It was found that the calculated distributions generate attractor-like structures in the (Z,σ_2) plane. More analysis will be performed in the future.

ASSESSING UNCERTAINTIES OF THEORETICAL ATOMIC TRANSITION PROBABILITIES WITH MONTE CARLO RANDOM TRIALS

ALEXANDER KRAMIDA

National Institute of Standards and Technology, Gaithersburg, MD, USA

Suggested strategy for estimating uncertainties of theoretical calculations:

1) Investigate internal uncertainties of the model by varying its parameters and comparing results.
2) Investigate internal uncertainties of the method by extending the model and looking at convergence trends.
3) In some cases, a general estimate of internal uncertainties can be obtained by comparing results calculated in different gauges.
4) Investigate possible contributions of neglected effects.
5) Investigate external uncertainties of the method by comparing with results of other methods.

A Monte Carlo method is suggested for step (1). It is explained in detail in [1], where an implementation of this method with Cowan's suite of atomic codes [2] is explained. The key point of the method is the relation between the uncertainties in the values of Slater (energy) parameters $\boldsymbol{P}$ and the residual differences between experimental and theoretical energy levels $\boldsymbol{E}$,

$$\Delta\boldsymbol{P} = [\partial\boldsymbol{P}/\partial\boldsymbol{E}]\,(\boldsymbol{E}_{\mathrm{exp}} - \boldsymbol{E}), \tag{1}$$

in which the necessary element of the calculation is the matrix of derivatives $[\partial\boldsymbol{P}/\partial\boldsymbol{E}]$.

By randomly varying parameters $\boldsymbol{P}$ with distribution widths defined by Eq. (1), one obtains sets of results that can be compared to the initial data set to reveal statistical properties of the calculated quantities, such as shapes and widths of statistical distributions.

Such investigation of 590 M1 and E2 transition probabilities within the ground configuration of Fe V revealed that, for most of these transitions, statistical distributions are highly asymmetric and far from normal, with large number of extremely large deviations from the mean. Quantification of uncertainties, e.g., determination of confidence limits, is possible only if a suitable transformation function is applied to transition probabilities, so that the transformed quantity has nearly normal distribution. Due to strong asymmetries and presence of extremely large deviations from the mean of the distributions, dependable assessment of shapes and widths of the distributions requires a large number of data sets to be compared. If one wants to know the standard uncertainties of transition probabilities accurate within a factor of two, comparing ten data sets yields sufficiently accurate standard uncertainties for 90% of transitions.

References

[1] A. Kramida, *Assessing Uncertainties of Theoretical Atomic Transition Probabilities with Monte Carlo Random Trials*, Atoms **2**, 86–122 (2014); DOI:10.3390/atoms2020086

[2] R. D. Cowan, *The Theory of Atomic Structure and Spectra*, University of California Press, Berkeley, CA, 731 pp. (1981)

Nuclear Data Section
International Atomic Energy Agency
Vienna International Centre, P.O. box 100
A-1400 Vienna, Austria

E-mail: nds.contact-point@iaea.org
Fax: (43-1) 26007
Telephone: (43-1) 2600 21725
Web: http://www-nds.iaea.org