Uncertainty assessment for calculated atomic, molecular and nuclear data and implications for GUM

B. J. Braams, H.-K. Chung and R. Capote

Nuclear Data Section, Division of Physical and Chemical Sciences, International Atomic Energy Agency (IAEA), Vienna, Austria

Code Centre Network Meeting on Plasma-Material Interaction, IAEA, Vienna, 29-31 July 2015

(Based on Talk at BIPM Workshop on Measurement Uncertainty, Sèvres, Paris, 15-16 June 2015)

IAEA
International Atomic Energy Agency

Calculated data and measured data

Classification defined:

For present purposes it is *Calculated* or *Measured* data (or both) according to where is the main source of uncertainty.

Point acknowledged:

Measured data involve calculations (to go from instrument reading to measurand) and calculated data involve measured quantities (e.g. the values of fundamental constants and of many not so fundamental parameters).

Today's focus:

Calculated data. The calculations are the main source of uncertainty in the final result.

IAEA

Quantity of Interest (QOI) for calculated data

QoI for calculated data has special features.

- Often high-dimensional. A function rather than a number; e.g. a cross section as a function of energy; a differential cross section; an equation of state. In that case, uncertainties in the individual (scalar) components of the QoI are strongly correlated.
- Sometimes also measured. In atomic spectra: line positions and amplitudes.
- Often very hard or impossible to measure. State-specific cross sections; equation of state under extreme conditions.
- Sometimes doesn't make sense as a measured quantity. The Schrödinger wavefunction. Climate sensitivity.

IAEA

Three main classes of computations

Applied numerical analysis (NA): precisely specified problems typically belonging to linear algebra, optimization and approximation, differential equations, integral equations and to some extent stochastic systems.

Simulation of complex systems: basic equations may not be well established, may involve poorly known parameters and functional dependencies, include stochastic elements and may give rise to chaotic behaviour.

Calculations for simple systems that are computationally hard: prime examples are electronic structure and other many-body quantum mechanics; also problems in combinatorial optimization.

IAEA

Uncertainty assessment for the 3 classes

Applied numerical analysis: There is the concept of an exact value and of convergence of the numerical method and there is a theory of discretization error and rounding error; this is the core of classical numerical analysis. The field has no need for guidance from VIM and GUM.

Simulation of complex systems: Domain of Uncertainty Quantification (UQ); note SIAM and GAMM activity groups, meetings, NAS report, thrust area for support. Concern with uncertainty propagation for stochastic systems; “polynomial chaos.” The field of UQ can provide examples for GUM.

Calculations for simple systems that are computationally hard: Science of uncertainty assessment or UQ needs to be developed for specific applications.

Atomic, molecular, nuclear and surface (AMNS) data

IAEA Nuclear Data Section is concerned with nuclear data and also atomic, molecular and plasma-material interaction data.

Nuclear data: Dominated by models that are evaluated or calibrated with reference to experimental data.

Atomic and molecular data: Major role for calculated data based on electronic structure theory; simple physical systems that are computationally hard.

Plasma-material interaction data: Both calculated and measured data; calculations have some flavour of those for “complex systems.”

IAEA

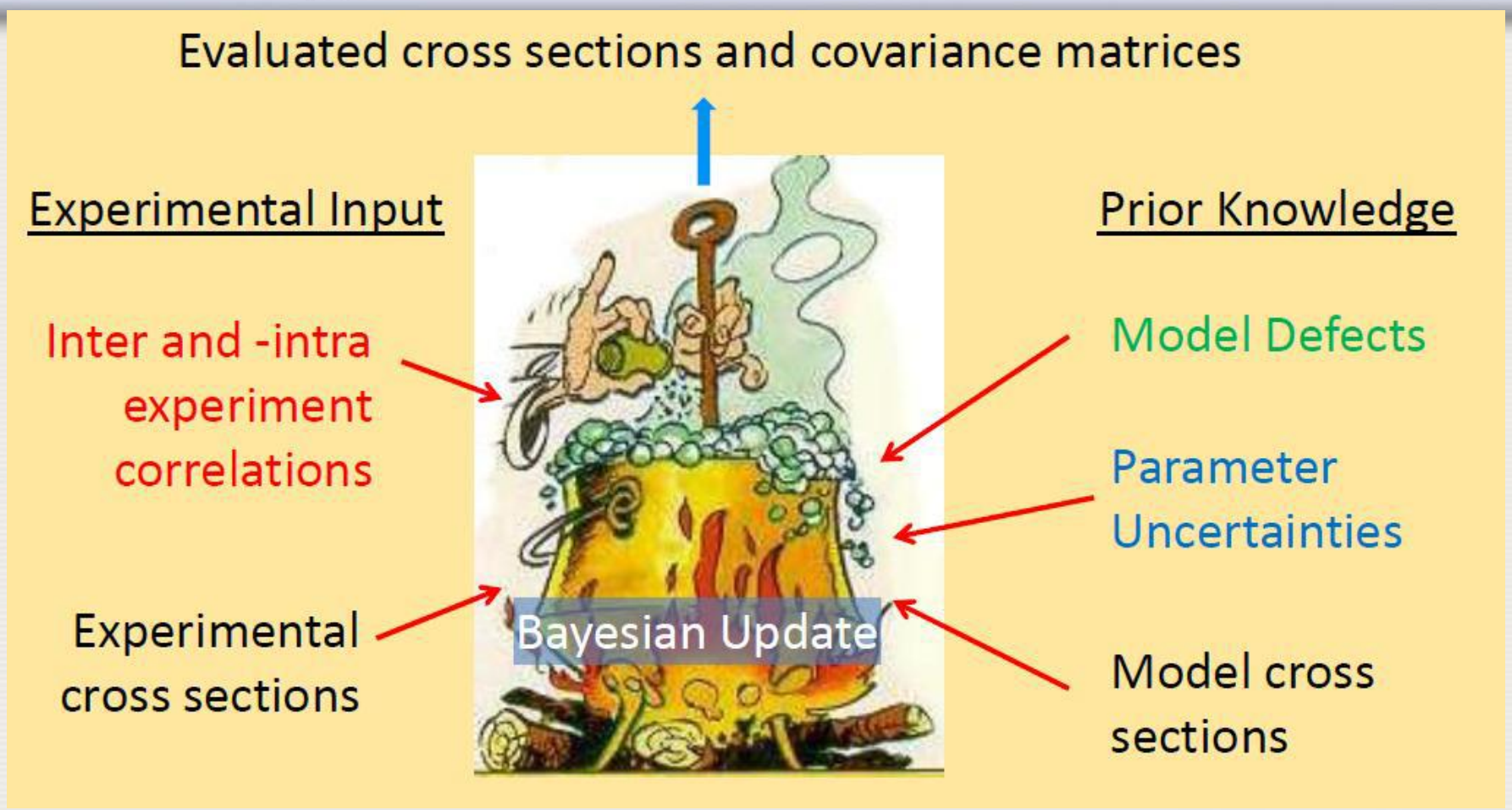
Nature of calculations for AMNS data

First principles calculations: In general it means, no tunable parameters. In the context of A+M physics it means calculations based on the many-body Schrödinger equation. Mainly relevant for atoms and small molecules.

Less than first principles: Tunable parameters, but experiment is in the background (e.g., parameters have been tuned in some transferable way). Density functional theory (DFT) for large molecules and condensed phase; general force fields.

Based on models: Calibrated to experimental data. Includes all of nuclear physics: structure, decay, scattering. (Lattice QCD would be first principles.)

Unified Monte Carlo Approach for Nuclear Data



From D. Neudecker, S. Gundacker, H. Leeb et al., ND2010, Jeju Island, Korea;
Via R. Capote, presentation at IAEA, 2013-05-06

IAEA

Unified Monte Carlo Approach for Nuclear Data

Following R. Capote, presentation at IAEA, 2013-05-06

- $p(\sigma) = C \times \mathcal{L}(y_E, V_E \mid \sigma) \times p_0(\sigma \mid \sigma_C, V_C)$
- $p_0(\sigma \mid \sigma_C, V_C) \sim \exp\{-(\frac{1}{2})[(\sigma-\sigma_C)^T \bullet (V_C)^{-1} \bullet (\sigma-\sigma_C)]\}$
- $\mathcal{L}(y_E, V_E \mid \sigma) \sim \exp\{-(\frac{1}{2})[(y-y_E)^T \bullet (V_E)^{-1} \bullet (y-y_E)]\}$, $y = f(\sigma)$
- y_E, V_E: measured quantities with *n* elements
- σ_C, V_C: calculated using nuclear models with *m* elements

Use Metropolis (Markov chain) sampling for σ.

[] D. L. Smith, "A Unified Monte Carlo Approach to Fast Neutron Cross Section Data Evaluation," Proceedings of the 8th International Topical Meeting on Nuclear Applications and Utilization of Accelerators, Pocatello, Jul 29 – Aug 2 2007, p. 736.

[] R. Capote and D. L. Smith, "Unified Monte Carlo and Mixed Probability Functions," Journal of the Korean Physical Society 59 (2), August 2011, pp. 1284-1287 (Proceedings ND2010).

IAEA

Contribution from IAEA A+M Data Unit

Our task: To provide internationally recommended and validated data for A+M+PMI/PSI processes relevant to fusion.

Challenge: Develop practical methods to estimate uncertainties of calculated data.

Meeting highlight: IAEA-ITAMP Technical Meeting on Uncertainty Assessment for Theoretical Atomic and Molecular Scattering Data, Cambridge, MA, 7-9 July 2014.

This presentation: General survey; Unified Monte Carlo for nuclear data; lower bound approach for electronic structure.

Call for a new discipline: Uncertainty Quantification for simple physical systems that are computationally hard.

IAEA

Editorial statement, *Phys Rev A* (2011)

Papers presenting the results of theoretical calculations are expected to include uncertainty estimates […] especially under the following circumstances:

- If the authors claim high accuracy, or improvements on the accuracy of previous work.
- If the primary motivation for the paper is to make comparisons with [high precision measurements].
- If the primary motivation is to provide interpolations or extrapolations of known experimental measurements.

In practice: Policy works well for calculated structure data, not so well for calculated scattering data. (For structure data spectroscopy provides experimental benchmarks.)

IAEA

Lower-bound method for electronic structure

The reduced density matrix method for electronic structure calculations and the role of three-index representability conditions

Zhengji Zhao[1], Bastiaan J. Braams[2], Mituhiro Fukuda[2], Michael L. Overton[3] and Jerome K. Percus[4]

+ VIEW AFFILIATIONS

J. Chem. Phys. **120**, 2095 (2004); http://dx.doi.org/10.1063/1.1636721

The variational approach for electronic structure based on the two-body reduced density matrix is studied, incorporating two representability conditions beyond the previously used $\mathbf{P}$, $\mathbf{Q}$, and G conditions. The additional conditions (called $\mathbf{T1}$ and $\mathbf{T2}$ here) are implicit in the work of Erdahl [Int. J. Quantum Chem. **13**, 697 (1978)] and extend the well-known three-index diagonal conditions also known as the Weinhold–Wilson inequalities. The resulting optimization problem is a semidefinite program, a convex optimization problem for which computational methods have greatly advanced during the past decade. Formulating the reduced density matrix computation using the standard dual formulation of semidefinite programming, as opposed to the primal one, results in substantial computational savings and makes it possible to study larger systems than was done previously. Calculations of the ground state energy and the dipole moment are reported for 47 different systems, in each case using an STO-6G basis set

Key Topics

- Optimization
- Computational methods
- Configuration interaction
- Coupled cluster
- Electric dipole moments

Summary remarks: NA vs UQ

Numerical Analysis deals with precisely specified problems.

- There is a concept of an exact answer.
- One studies discretization error, truncation error.

Electronic structure has NA aspects.

- (one electron) basis set extrapolation.
- R-matrix convergence wrt radius.

Complexity of electronic structure goes beyond NA.

- Cannot extrapolate to Full CI limit.
- Must rely on models, e.g. DFT.
- Most difficult: electronic excitation and condensed matter.

IAEA

Summary remarks: calculated data in GUM

In the present GUM: Uncertainties in calculated data are basically out of scope. If calculations can be described as experiments then elements of GUM could apply, but examples are not developed.

In a revised GUM: Questionable.

I don't expect that a practitioner that uses tools from numerical analysis will look to GUM-rev for the uncertainty assessment.

Probably GUM-rev can benefit from a close look at UQ and use it as a source of examples. Probably GUM-rev should refer to tools of UQ; beyond that, I don't know.

The uncertainty assessment for computationally hard simple systems needs real science development.

IAEA