Steps Towards Uncertainty Estimates for Calculated Atomic and Molecular Data

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International Atomic Energy Agency

Introduction

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

Uncertainty assessment is well established for experimental data; needs work for theoretical data.

Challenge: Develop methods to estimate uncertainties of calculated data that do not require huge additional computational effort.

This presentation: One approach from the nuclear data community; Unified Monte Carlo.

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

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Editorial Statement, *Phys Rev A* (2011)

Papers presenting the results of theoretical calculations are expected to include uncertainty estimates for the calculations whenever practicable, and 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 present or future high precision experimental 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.)

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Verification, Validation and UQ

Verification. The process of determining how accurately a computer program ("code") correctly solves the equations of the mathematical model.

Validation. The process of determining the degree to which a model is an accurate representation of the real world from the perspective of the intended uses of the model.

Uncertainty quantification (UQ). The process of quantifying uncertainties associated with model calculations of true, physical QOIs, with the goals of accounting for all sources of uncertainty and quantifying the contributions of specific sources to the overall uncertainty.

See NRC Report "Assessing the Reliability of Complex Models: Mathematical and Statistical Foundations of Verification, Validation, and Uncertainty Quantification" (NAP, 2010 online).

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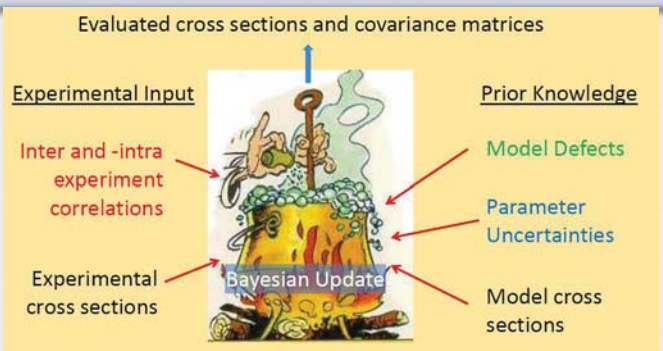
Unified Monte Carlo Approach for Nuclear Data



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

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Unified Monte Carlo Approach for Nuclear Data

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

- $p(\sigma) = C \times \mathcal{L}(y_E, V_E \mid \sigma) \times p_0(\sigma \mid \sigma_C, V_C)$
- $p_0(\sigma \mid \sigma_C, V_C) \sim \exp\{-(\tfrac{1}{2})[(\sigma-\sigma_C)^T \cdot (V_C)^{-1} \cdot (\sigma-\sigma_C)]\}$
- $\mathcal{L}(y_E, V_E \mid \sigma) \sim \exp\{-(\tfrac{1}{2})[(y-y_E)^T \cdot (V_E)^{-1} \cdot (y-y_E)]\}$, $y = f(\sigma)$
- y_E, V_E: measured quantities with n elements
- y_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).

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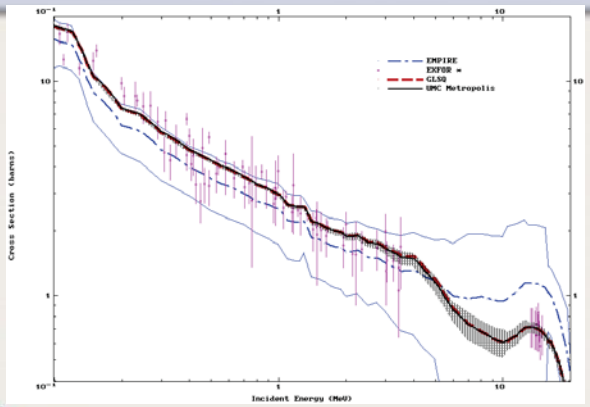
Unified Monte Carlo Approach for Nuclear Data



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Outline of UMC for Rovibrational Spectroscopy

Starting point: MULTIMODE code

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Taylor & Francis
Taylor & Francis Group

MULTIMODE: a code to calculate rovibrational energies of polyatomic molecules

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This review focuses on the calculation of rovibrational energies of polyatomic molecules using the code MULTIMODE. This code, which uses normal coordinates and a hierarchical n-mode representation of the potential, aims to be applicable to a wide class of molecules and molecular complexes. The theoretical and computational methods used in this code are described, followed by a review of selected applications. These applications illustrate various features of the code and also point out some limitations of the current version of the code. The review concludes with some ideas about possible future directions in this area of research.

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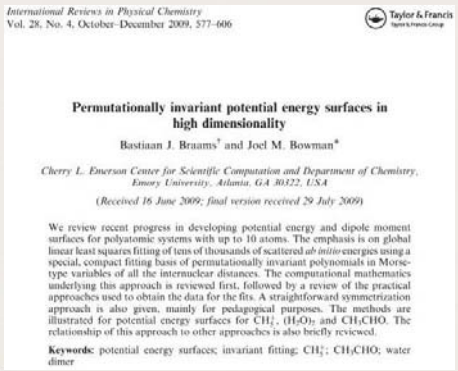
Outline of UMC for Rovibrational Spectroscopy

Auxiliary tool: Potential Energy Surface (PES) fitting procedures



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Taylor & Francis

Permutationally invariant potential energy surfaces in high dimensionality

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We review recent progress in developing potential energy and dipole moment surfaces for polyatomic systems with up to 10 atoms. The emphasis is on global linear least squares fitting of tens of thousands of scattered *ab initio* energies using a special, compact fitting basis of permutationally invariant polynomials in Morse-type variables of all the internuclear distances. The computational mathematics underlying this approach is reviewed first, followed by a review of the practical approaches used to obtain the data for the fits. A straightforward symmetrization approach is also given, mainly for pedagogical purposes. The methods are illustrated for potential energy surfaces for CH_5^+, $(H_2O)_2$ and CH_3CHO. The relationship of this approach to other approaches is also briefly reviewed.

Keywords: potential energy surfaces; invariant fitting; CH_5^+; CH_3CHO; water dimer

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Outline of UMC for Rovibrational Spectroscopy

Rovibrational molecular spectrum is obtained from solution of the nuclear Schrödinger equation:

$$-\frac{\hbar^2}{2M}\Delta\Psi + V\cdot\Psi = E\cdot\Psi$$

Here, Ψ is the nuclear wavefunction (say for N nuclei) and $V(x)$ is the solution of the electronic S.E. for nuclear configuration x (Born-Oppenheimer approximation).

Watson hamiltonian: expansion in rotational states leaving $3N-6$ independent nuclear coordinates.

Solution of nuclear S.E. (eigenvalue problem) provides spectrum and (dipole, etc.) matrix elements.

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Outline of UMC for Rovibrational Spectroscopy

Sources of error and uncertainty

- Ab initio electronic structure calculations
- Fitted potential energy surface
- Solution of nuclear Schrödinger equation
- Validity of Born-Oppenheimer approximation

Approach via Unified Monte Carlo

- Treat the PES as the model prior
- MULTIMODE supplies the posterior
- Need some accurate lines to evaluate likelihood of the posterior

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Outline of UMC for Rovibrational Spectroscopy

Prior:

Consider a linear model for ease of exposition. The coefficients c_i are uncertain.

$$V(x) = \sum_i c_i\, f_i(x)$$

$$c = c^{(0)} + Gaussian(0, M)$$

(Dispersion matrix M may be obtained along with least squares determination of $c^{(0)}$.)

If a nonlinear model is used, or a more complicated expression for the prior uncertainty, then one may need Metropolis sampling to obtain c. In practice the model for V may have a few nonlinear and many linear parameters; then combine Metropolis and analytical.

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Outline of UMC for Rovibrational Spectroscopy

Posterior:

For any coefficients c sampled from the prior

- Set up and solve the nuclear Schrödinger equation [*];
- Evaluate rms deviation for selected known lines;
- Evaluate likelihood; accept or reject vector c.

Evaluate complete $spec(H)$ and relevant matrix elements *and an estimated uncertainty* from the (Metropolis) statistics.

[*] Maybe solve the S.E. only once, for a reference vector *c*, and then assume a linear response to changes in *c*.

For consideration: Could anything similar work for scattering data?

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Uncertainty Quantification for physically simple, computationally hard systems

Uncertainty Quantification (UQ) is a burgeoning field.

- National Research Council Committee on Mathematical Foundations of Verification, Validation, and Uncertainty Quantification: …, 2012.
- SIAM and GAMM Activity Groups on Uncertainty Quantification.
- Prominent in NSF DMS (and at other funding agencies, I assume).

Almost totally devoted to complex systems.

- Stochastic systems, chaotic behavior, e.g. atmosphere-ocean system.
- Engineering processes in complicated geometry, e.g. combustion.
- Radiation hydrodynamics with many species and processes.

An atom or small molecule is a simple system.

- Collision processes are physically simple.
- Stochastic process generally not chaotic, e.g. Auger cascade.

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Numerical Analysis 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.

Challenge for future work to improve UQ

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