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Editorial

Notes on Critical Assessment of Theoretical Calculations of Atomic Structure and Transition Probabilities

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Abstract: Atomic structure and transition probabilities are fundamental physical data required in many fields of science and technology. Atomic physics codes are freely available to other community users to generate atomic data for their interest, but the quality of these data is rarely verified. This special issue addresses estimation of uncertainties in atomic structure and transition probability calculations, and discusses methods and strategies to assess and ensure the quality of theoretical atomic data.

Keywords: atomic structure; atomic transition probability; data evaluation

1. Introduction

Atomic structure and transition probabilities are widely used in many diverse fields of science and technology, from atomic spectroscopy for diagnostics to modelling of exotic matter states generated in laboratory experiments or in astrophysical objects. Many applications require extensive sets of atomic structure and transition probability data beyond a few strongest lines accessible by measurements. Due to great advances in computational capabilities and computational atomic physics, there are codes available in the community that allow a complete set of atomic data to be generated without an heroic effort. While a demand to obtain atomic data is readily met with data from available codes, the quality

of data is difficult to assess for a user without much knowledge of atomic physics. In most cases, the user-generated data is unlikely to be verified by experts, and may lead to unsatisfactory results.

The need for data verification is even greater as applications of atomic data become more elaborate and complex, and hence require higher quality data. A list of critically evaluated atomic structure and transition probabilities data exists in the databases of the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) [1], although thus far in a rather limited volume. Recently, there has been an effort to enhance community activities in evaluating, and critically assessing atomic and molecular data for applications [2,3]. Critical evaluation of data is challenging, since only a limited number of benchmark experiments exist and one has to rely heavily on theoretical estimates. In particular, theoretical data are rarely provided with uncertainty estimates, which makes an evaluation of theoretical data even more difficult.

It is not immediately obvious how to give a quantitative estimate of the uncertainty of a theoretically or numerically obtained value. There seems to be no straightforward answer or recipe; however, it is important for code developers and users to identify sources of uncertainties in their code results and develop ways to ensure the quality of numerically generated data. With this special issue, we would like to address ways to estimate uncertainties of calculated atomic structure and transition probabilities, and assure the quality of theoretical atomic data.

2. Ideas and Suggestions

Uncertainty estimates of theoretical atomic data depend on the complexity of the atomic system, computational methods, and the number of different states. Calculations for a few states and "spectrum" calculations for massive sets of transition data should be different.

The wave function for a state in multi-configuration methods is expanded in configuration state functions (CSFs), which are symmetry adapted and anti-symmetrized products of one-electron orbitals. Given approximate wave functions for the initial and final states, transition parameters such as line strengths, can be evaluated in length and velocity gauges (or Babushkin and Coulomb gauges in relativistic calculations). Differences between the transition parameters calculated in the different gauges can be used as uncertainty estimates. For *LS*-allowed transitions Froese Fischer suggested [4] that the uncertainty $\delta A'$ in a transition rate A' may be estimated by

$$\delta A' = (\delta E + \delta S)\, A', \tag{1}$$

where

$$\delta E = |E_{(obs)} - E_{(cal)}|/E_{(obs)} \tag{2}$$

and

$$\delta S = |S_{(length)} - S_{(velocity)}|/\max(S_{(length)};\, S_{(velocity)}) \tag{3}$$

are, respectively, the uncertainties in the transition energy and line strength. The above uncertainty estimate cannot directly be applied to *LS*-forbidden transitions. Different generalizations are, however, possible.

The uncertainties of transition data may also be inferred from convergence studies. A model for generating CSFs from the one-electron orbital basis may be defined and the one-electron orbital basis

can be increased in a systematic way to monitor the convergence of the transition parameters. Converged values may be obtained with several models of different electron correlation effects, and uncertainties may be estimated for the convergence of transition parameters within each model as well as between models. The limitation for this study would be the rapid growth of the number of CSFs, which makes it difficult to establish converged values for some cases. It would be difficult to give an estimate for systems beyond models that account for valence and core-valence correlation.

The wave functions may be "fine-tuned" by shifting diagonal elements in the Hamiltonian to reproduce the measured energy separations. In some cases the sensitivity of the transition parameters to the tuning may be used for estimating uncertainties. This method is not available, however, for fully relativistic calculations in *jj*-coupling, where off-diagonal elements in the Hamiltonian matrix may be large.

For "spectrum" calculations, internal benchmarking can be applied to estimate uncertainties. Internal benchmarking amounts to performing very accurate and elaborate calculations for a few carefully selected transitions. The results from the less accurate "spectrum calculation" are then compared against values from the internal reference transitions for uncertainty estimates.

3. Summary

The need for critical assessment of theoretical calculations of atomic structure and transition probabilities, and some suggestions, are presented.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

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