

Uncertainty assessment for calculated atomic, molecular and nuclear data for fusion and nuclear applications

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Abstract – *The uncertainties of the outputs of global or integrated modeling of fusion and other nuclear applications depend on uncertainties of input parameters as they propagate through the simulation. Hence, there is an increasing interest in quantifying uncertainties of fundamental reference data such as atomic, molecular and nuclear energy levels, transition rates, branching ratios and scattering cross sections, as well as reference data for particle-surface and plasma-material interaction processes. In the nuclear data community and in experimental atomic and molecular science this is a well-established area of research, but uncertainty quantification is much less developed for the case of strictly calculated atomic, molecular and plasma-material interaction data. The topic of this conference contribution is the status of uncertainty quantification of fundamental atomic, molecular, nuclear and plasma-material interaction data for fusion and other plasma and nuclear applications. For the case of nuclear data we highlight methods based on Bayesian Monte Carlo to derive uncertainty estimates and their correlation structure from nuclear models together with experimental data. The use of focal point analysis for uncertainty quantification of structure data is reviewed and additional difficulties for uncertainty quantification of calculated scattering data are discussed. For particle-surface and plasma-material interaction data the central role of molecular dynamics simulations and the propagation of uncertainties in the underlying force field is emphasized. We hope to motivate and challenge mathematical and computational communities to collaborate with atomic and molecular data communities and to develop applicable methods of uncertainty quantification for calculated fundamental structure and collision data for fusion and other plasma and nuclear applications.*

I. INTRODUCTION

Magnetic confinement fusion energy research is advancing towards the next generation of large experiments, with the stellarator Wendelstein-7X and the JT60-SA tokamak, respectively followed by ITER. Whereas Wendelstein-7X and JT60-SA are on the scale of earlier tokamak experiments (TFTR, JET and JT-60) ITER is very much larger and it is the first experiment in which extended fusion operation in D-T plasma is to be achieved.

Heat exhaust, control of plasma composition, material lifetime and tritium inventory are critical interlinked issues for the success of fusion energy production and for the success of the ITER experiment. The key to successful operation of ITER is to achieve stable operation with a high density, low temperature plasma (electron densities $\approx 1 \times 10^{21}/\text{m}^3$ and electron temperatures in the range 1-10 eV) in the divertor region where the most severe plasma-material interaction takes place. A part of the strategy may be the deliberate introduction of light impurities such as N, Ne or Ar in order to create a radiating mantle. In the low temperature divertor plasma neutral atoms and molecules will be present and in some regions the plasma can make a transition to a hot neutral gas state.

Atomic, molecular and plasma material interaction processes have a central position in the description of the edge plasma. The processes include line radiation by atomic impurities, formation of molecules (including impurity hydrides) on the walls and in the plasma, electron-atom

(ion), electron-molecule and heavy particle collisions, photon-induced processes including radiation transport, physical and chemical sputtering of surfaces, penetration and retention of plasma particles (especially tritium) in the walls, and evolution of the wall material.

Although the importance of atomic, molecular and plasma-wall interaction processes is well recognized there does not exist at present a generally accepted, validated and internationally recommended comprehensive library of relevant basic collision data. For molecular processes involving hydrogen, helium and light element impurities there is a great need to assemble the available data, critically assess their uncertainties, interpolate and extrapolate data in suitable ways to all parameter regimes of interest and provide recommended best data for use in plasma modelling. For plasma-material interaction there are significant gaps still in the basic data for relevant mixed materials, material after radiation damage and material that is exposed to a high plasma flux.

Uncertainty assessments are well established ingredients of experimental science, but much less so for computational research. However, the present database for collisional atomic and molecular processes relevant to fusion is almost entirely based on theory, due to the need to obtain data that is resolved with respect to electronic and molecular excitations. Atoms and small molecules may not be complex systems, but it is computationally hard to solve the many-body quantum mechanics governing the system. For these simple physical systems that are of high

computational complexity a new science of uncertainty assessment needs to be developed, or at least a new branch of the developing science of uncertainty quantification (UQ).

The procedure of quantifying uncertainties of nuclear structure and nuclear reactions, on the other hand, is well defined based on applications of the Bayes theorem and the Unified Monte Carlo (UMC) method [1-4]. Fundamental nuclear data are routinely evaluated with given uncertainties and correlations based on measured data combined with theoretical nuclear models [5]. There is an active research in improving mathematical and computational methods for UQ of nuclear data.

In this paper, we review methods used to estimate uncertainties of nuclear structure and reaction data and the current status of uncertainty quantification methods employed for theoretical atomic and molecular data largely based on the recent review paper [6].

II. UNCERTAINTY ESTIMATES OF NUCLEAR DATA

With the currently available computer power, probably the most general way to deal with uncertainty quantification (UQ) is to apply a combination of Bayesian statistics and Monte Carlo sampling. Bayesian Monte Carlo (BMC) [4] is a particular implementation of the Unified Monte Carlo method (UMC-B) [3], where a general way of defining a *prior* is implemented. The BMC can be seen as a gradual inference process in which the system slowly but surely learns about the optimal model parameters when nuclear model calculations are compared with experimental data.

In this case, the input to the Bayesian equation is:

1. A very uninformative prior, meaning nuclear model calculations undertaken with a very large uncertainty as *a priori* probability distribution of the parameters, i.e., not knowing of any experimental data.
 2. A likelihood function, representing the probability that the experimental data are reproduced if we assume that the nuclear model parameters are perfect. From the principle of maximum likelihood follows that this is proportional to $\exp(-\chi^2)$ where χ^2 is a generalized mean-square "distance" between calculated model points and measured data that may consider both uncertainties and experimental correlations [1-3].
 3. A posteriori probability distribution of the model (parameters) given the experimental data.
- One can include an extra step in this inference process by first applying a global model parameter set before one zooms into a local set for one particular isotope.

1. Experimental Data

The nuclear science community compiled experimental data in a standardized format in a library called EXFOR system [7] over a few decades. It is known that the evaluation is sensitive to bad (and discrepant) data and there

was a project by a subgroup of the NEA Working Party for Evaluation Cooperation (WPEC) to improve the data in EXFOR database [8]. Experimenters are encouraged to provide detailed information on their measurement in documentation and credible uncertainty estimates. Finally correlations between uncertainties of experiments are very important but not readily provided. The correlation information is critical for uncertainty estimation for evaluated data.

2. Nuclear Modeling

There are two sources of uncertainties in nuclear modeling: 1) Nuclear model parameter uncertainties and 2) Nuclear model deficiency uncertainties. For nuclear model parameter uncertainties, the initial parameter estimates and their uncertainties can be adopted from the Reference Input Parameter Library (RIPL) [9]. Uncertainties in the model parameters provide input for estimating the uncertainties of evaluated data. Uncertainties associated with the deficiencies in nuclear model contribute significantly to the overall uncertainties of nuclear models, however, it is not straightforward to assess since the deficiency arises from approximations or the lack of understanding. To estimate uncertainties associated with model deficiency, discrepancies between model calculations and good experimental results were examined. The model deficiency will be always speculative and correlations in these uncertainties will not be known.

The nuclear model code TALYS provides theoretical nuclear quantities, models and parameters with a reasonable accuracy for energy ranges of several keV and higher. It has been validated over 10-15 years. Fig. 1 shows probability distributions of optical model parameter r_v from the TALYS code using a BFMC approach [10]. The prior knowledge is a uniform distribution and gradually inserting more knowledge (obtained by comparing random parameter sets with experimental data) model parameter distributions may become peaked with reduced uncertainty.

3. Nuclear Data Evaluation

Stochastic (Monte Carlo) evaluation methods are widely used in nuclear data evaluation [5]: 1) Filtered Monte Carlo (FMC), 2) Unified Monte Carlo (UMC) [1-4], 3) Hybrid method of MC+GLSQ (e.g., Ref. [11]), 4) Backward-Forward Monte Carlo (BFMC) [10] and 5) Total Monte Carlo (TMC) [12]. In the FMC approach, a set of nuclear model parameters is generated by random sampling and hence the evaluation is mainly done on nuclear model parameters and their uncertainties. The UMC approach is more rigorous [1-4] than the FMC approach as experimental information including correlations is considered for mean values and uncertainties. The UMC approach combines Bayes Theorem and the Maximum Entropy Principle within a stochastic Monte Carlo approach. The Hybrid method uses

the model uncertainties to estimate the model prior and employs the deterministic GLSQ (Generalized least-squares) method to combine weighted experimental and model covariance matrices [11]. The BFMC approach [10] consists of two-steps: the Backward phase to determine the model parameter covariance matrix and the Forward phase to determine cross-section covariances by MC sampling. The TMC method extends the FMC approach to generate mean values and uncertainties of nuclear data of interest [12]. In addition, many refinements in MC approach coupled to Bayesian theorem are taken into account in practical implementations including any known uncertainty correlations within and between experiments (FBET, BMC, GANDR, KALMAN, etc).

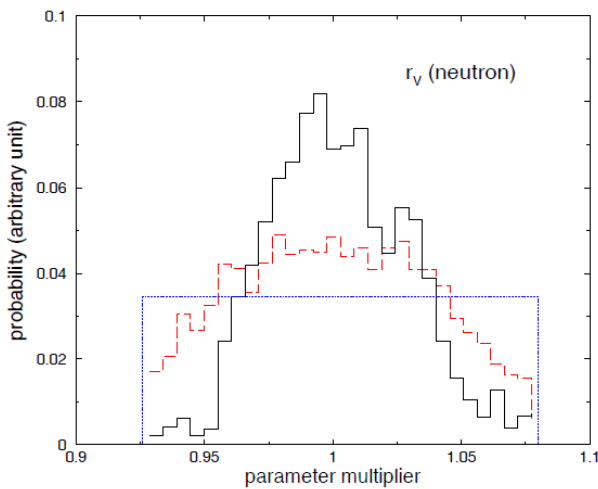


Fig. 1. Probability distribution for the TALYS parameter $r_{v,neutron}$: initial uniform distribution (blue), posterior distribution using pseudo-experimental data (red), and posterior distribution using experimental data for ^{90}Zr (black). The figure was taken from [4].

As an example, evaluated data sets of $^{55}\text{Mn}(n,\gamma)$ cross-section are demonstrated in the Fig. 2 evaluated with UMC-G [1-3] where the Unified Monte Carlo (UMC) evaluation is compared with evaluated data using GLSQ (Generalized Least Square) fit method. Both evaluated data used the same input: experimental data from EXFOR (Experimental Nuclear Reaction Data, IAEA) database [7] as well as random model calculations (as *prior*) with the nuclear reaction model code EMPIRE.

Recently, the UMC approach has been further developed for more general cases where the prior or the likelihood function is not a normal distribution with respect to variables corresponding to the model calculations. It has been shown that valuable shape information in the higher-order moments of the actual probability function may be lost due to the assumption of normal distribution of the prior

probability function. The new approach called UMC-B [3] generates a Markov Chain of observables values based on the prior probability function and retains all features of the underlying probability function associated with the derived observable variables. A similar approach is being applied with a particular choice of *prior* and called Bayesian MC [4].

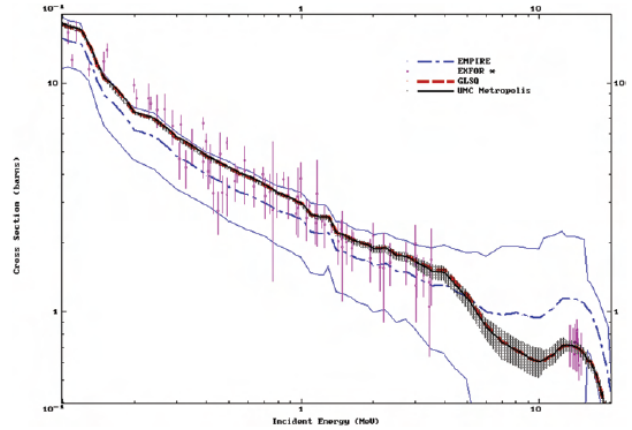


Fig. 2. Evaluated data and its uncertainties of $^{55}\text{Mn}(n,\gamma)$ cross-section using UMC and GLSQ evaluation methods compared with experimental data from EXFOR database and model calculations used as *prior*. The figure was taken from [3].

III. UNCERTAINTY ESTIMATES OF ATOMIC AND MOLECULAR DATA

1. Overview

The provision of uncertainty estimates for calculated atomic and molecular data is of rather recent interest and procedures for uncertainty quantification are much less developed for atomic and molecular data than they are for nuclear data. There are good reasons for this state of affairs in that in most of atomic and molecular physics one actually has a definite target for the calculations, viz. the solution of an appropriate many-body quantum system with known (Coulombic) interactions, whereas the nuclear data field is more reliant on models that are to be calibrated to experimental data. Here, largely following [6] we review approaches to estimate uncertainties associated with theoretical methods to calculate atomic and molecular data.

The fundamental equations for properties and processes considered in this review are those of quantum mechanics, always for a many-body system and generally including some treatment of effects beyond the classical non-relativistic Schrödinger equation. There are several sources of uncertainty in such calculations. They are additive in some sense, but depending on the application some are significant contributors to the final uncertainty and others are irrelevant.

A. Uncertainty in fundamental parameters, such as the fine structure constant and the electron-to-proton mass ratio, and in nuclear properties outside the domain of atomic physics, such as the mass, magnetic dipole moment, electrostatic quadrupole moment and finer details of the charge distribution of nuclei involved in the system under consideration

There are very few systems for which calculations can be done to such high accuracy that the uncertainty in fundamental constants, or in the nuclear masses, plays any role, and these specialized calculations are outside the scope of this review. The uncertainties in the nuclear magnetic dipole moments, quadrupole moments and charge radius can be significant in atomic spectroscopy, and indeed atomic spectroscopy is a route to the measurement of these parameters. There are some specialized works in computational spectroscopy of diatomic molecules for which the uncertainty in the nuclear magnetic dipole moment, electrostatic quadrupole moment or charge radius is an issue, but for most applications in molecular spectroscopy these uncertainties in nuclear properties make an insignificant contribution to the total uncertainty of the calculations. For scattering cross sections at energies relevant to this review (below the MeV energies used for probing nuclear structure) the uncertainties in nuclear properties are completely irrelevant relative to the total uncertainty due to approximations in the calculation.

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

Leaving aside any dreams of a final theory, which is not our field, we are concerned here with various approximations at the level of the basic equations. In atomic structure theory (atomic spectroscopy and transitions) the treatment of relativistic contributions to the Hamiltonian can make an important contribution to the total uncertainty; this is discussed further in Sec. 3.2. For molecular systems the separation between nuclear and electronic degrees of freedom (the adiabatic or Born-Oppenheimer approximation), or the treatment of effects beyond the adiabatic approximation, creates uncertainty that is in practice much harder to control than the uncertainty due to relativistic terms in the Hamiltonian.

C. Uncertainty in the model for many-body quantum mechanics

The nonrelativistic many-body Schrödinger equation is intractable at a fundamental level, and some model must be introduced even before numerical discretization. At the fundamental level the equation can be discretized in a space of Slater determinants and in that form the complexity of the algebraic eigenvalue problem is determined by two parameters: the number of electrons, N , and the size of the

one-electron basis, r . In terms of these parameters the number of determinants and the dimension of the eigenvalue problem is $r!/((r-N)!N!)$, which scales as r^N if $r \rightarrow \infty$ for fixed N , and scales exponentially with N as $N \rightarrow \infty$ for a fixed ratio $r/n > 1$. Thus, the “full configuration interaction” treatment of the many-body Schrödinger equation is computationally intractable already for quite small systems such as the CO₂ molecule with its 22 electrons. This aspect of formal intractability (exponential scaling of computational cost as a function of a natural measure of problem size) sets electronic structure theory apart from many other fields of computational science, such as computational fluid dynamics. For the case of electronic structure theory one is always forced to use a reduced description by which the exponential scaling of computational cost is replaced by something tractable. The reduced description can be an essentially one-electron model such as Hartree-Fock (HF) or density functional theory (DFT), or a few-electron model such as a coupled cluster (CC) expansion or a truncated configuration interaction.

D. Uncertainty due to discretization of the model equations

The selected model for the many-body quantum system must be discretized, which usually involves the choice of a finite basis of atomic orbitals for atomic and molecular systems or a Fourier-space discretization in the case of electronic structure calculations for condensed phase. Truncation of the basis introduces a numerical error relative to the complete basis limit. In practice the computational cost often scales as a high power of the size of the basis and the truncation error is a significant source of uncertainty.

E. Uncertainties beyond the quantum mechanical treatments

In the previous paragraphs we discussed sources of uncertainty introduced by the need to approximate many-body quantum theory, but finally problems of scattering theory are often reduced to classical calculations; for example trajectory calculations using Newton’s equations for motion of nuclei (molecular dynamics) with use of an interaction potential that has been fitted to electronic structure calculations or that has been calibrated some other way. The representation of the potential is now an important source of uncertainty that is difficult to quantify. (The need to sample from many trajectory calculations is another source of uncertainty, but it is much easier to control.)

In the remainder of this section we summarize tools to estimate uncertainties such as focal point analysis (FPA) techniques [13] and standard methods of convergence analysis for the numerical uncertainties for atomic and molecular structure data, and discuss examples of obtaining uncertainties of electron scattering data with atoms and molecules and charge transfer collisions between atoms and ions largely following the paper [6].

2. Atomic and Molecular Structure

The atomic structure of hydrogen can be exactly solved for nonrelativistic wave function and energy. In this case, the uncertainties are attributed to correction terms such as relativistic corrections and quantum electrodynamic (QED) corrections as well as the effects of finite nuclear size and structure. Among these, QED corrections (Lamb shifts) present a dominant source of uncertainties of order $(\alpha^4 Z^4)$ Ry where α is fine structure constant of $1/137.035999139(31)$ and Z is the nuclear charge.

For more than two electron systems, the Schrödinger equation cannot be solved exactly and uncertainties associated with electron correlation dominate relativistic corrections for $Z \leq 27$ where the nonrelativistic Schrödinger equation is solved for a best possible solution to include all electron correlations and relativistic corrections are treated as a perturbation. The correlation energy is the difference between the exact energy and the approximation using spherically averaged potentials in an independent particle approximation. For $Z > 27$, one-electron solutions to the Dirac equation is solved and electron correlation is treated as a perturbation. For two or three electron atoms, a Hylleraas basis set of functions provides solutions to the Schrödinger equation.

For non-relativistic multi-electron atoms, the Hartree-Fock approximation, or the multi-configuration Hartree – Fock (MCHF) or configuration interaction (CI) methods are used. For relativistic cases, Dirac equation is used as Dirac-Fock (DF) approximation. The key problem is to improve the correlation energy by solving systemically larger problems by allowing more electronic configurations to interact and improving the electrostatic potentials arising from electron repulsions (configuration mixing). In this case, the convergence of solutions with configuration mixing is the indicator of accuracy.

For molecular electronic ground state, Born-Oppenheimer (BO) approximation to separate nuclear and electronic motion is adopted as the main approximation. The correction terms consist of the potential energy surfaces (PES) which provide the link between electronic structure theory and nuclear motion theory and any BO corrections. One important distinction between atoms and molecules is that the molecular structure calculations aim for relative energies rather than the absolute total energy. Therefore it is the same for uncertainties.

Similarly to the atomic structure, three approximations exist in molecular electronic structure theory: choice of the electronic Hamiltonian, particle basis sets, correlation treatment. The composite Focal-Point Analysis (FPA) approach [13] is to use different levels of theory to calculate molecular structure properties to the *ab initio* limit and has been highly successful. The basic idea is to 1) use a family of basis sets (aug-cc-pVXZ etc) which are systematically changed to the completeness, 2) apply lower levels of theory

(typically, HF etc) with very extensive basis sets, 3) execute high order correlation treatments and 4) examine the added correlation increments.

The procedure is illustrated in Fig. 3. With the FPA approach, one can examine the uncertainties associated with electron correlation, relativity, QED as well as adiabatic and nonadiabatic corrections to the BO approximation. FPA-type approaches are also used to estimating uncertainties for permanent and transient dipole moments.

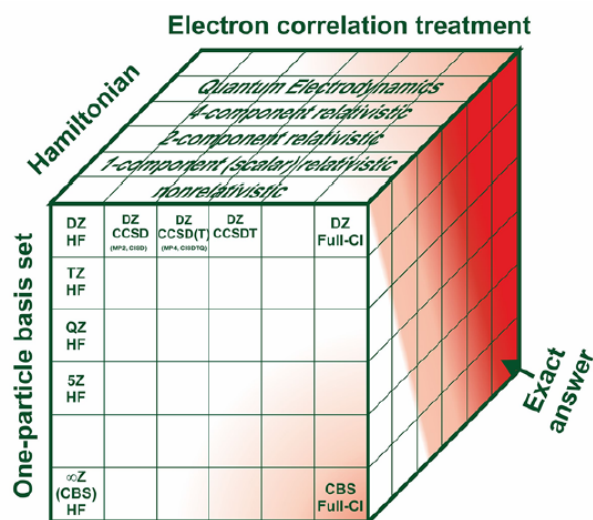


Fig. 3. Three axes of the computational aspects of Focal point analysis (FPA) technique to calculate electronic structure of molecules. The figure is from Ref. [2].

FPA approach has been used for excited electronic states, however, in a limited way. As molecular excited electronic states are often viewed as valence and Rydberg states, different techniques are used for these states. While quantum defect theory is well suited to describe Rydberg states, uncertainties in these states are often better described in terms of quantum defects rather than absolute energies.

The FPA method for uncertainty assessment of the calculated dissociation energy [14] of $H_2^{16}O$ is demonstrated in Table 1. The uncertainties of 1 cm^{-1} due to nonadiabatic effects are included.

Table 1. Ab initio contributions to the first dissociation energy of $H_2^{16}O$. All values are in cm^{-1} . Uncertainties are given in the last column. The table is from Ref. [6].

		Value	UQ
A	CBS CCSD(T) frozen core	43 956	6
B	Core correlation CCSD(T)	+81	2
C	All-electron CBS CCSD(T) [=A+B]	44 037	6
D	Higher order electron correlation	-52	3
E	CBS FCI [=C+D]	43 985	7

F	Scalar relativistic correction	-53	3
G	QED (Lamb shift) correction	+3	1
H	Spin-orbit effect	-69.4	1
I	Angular momenta coupling, OH	+31.5	0
J	Sum spin effects, OH [=H+I]	-37.9	1
K	DBOC, H ₂ O	+35.3	0.5
L	ZPE H ₂ O	4638.1	0
M	ZPE OH	1850.7	0.5
N	Net ZPE, H ₂ O [=L+M]	2787.4	0.5
U	Nonadiabatic contribution	0	1
V	Total MD, H ₂ O [=I+K+N+U]	-2721	1
	D ₀ (H ₂ O) Calc. [=E+V]	41 145	8
	(Obs—Calc) D ₀ (H ₂ O)	+1	-

3. Electron Collisions with Atoms and Molecules

Uncertainty estimates for scattering data are even less developed than structure data as they should include uncertainties of structures as well as reaction probabilities. In fact the uncertainties of structures propagate through to the uncertainties of scattering data. Also it should be noted that scattering dynamics change as a function of collision energy and hence one should apply different methods to calculate data of different energy ranges. There are 5 energy ranges of interest: 1) low energy collisions with incident projectile energies well below the threshold, 2) low energy at near threshold, 3) intermediate energy collisions with incident projectile energies between the 1st ionization threshold and a few times of that, 4) high energy collisions above a few times of the first ionization energy and 5) collisions with relativistic energies. As in the structure problem, the choice of Hamiltonian (relativity, QED etc), electron correlation, basis sets are important considerations for uncertainty quantification and the treatment of exchange effects between the projectile electron and target electrons is one of the key approximation to determine the accuracy of results.

As discussed further in Ref. [6], for low energy electrons, a one-state close-coupling expansion method is a reasonable approach as it contains exchange effects. At the near-threshold regime, the method of close-coupling (CC) expansion of a number of discrete states has been successful particularly describing resonances associated with low-lying inelastic thresholds. For intermediate energy collisions, the CC expansion to a large number of discrete states and ionization continuum states is required. The ‘convergent close-coupling’ (CCC) and ‘R-matrix with Pseudo-States’ (RMPS) approaches use a method called “pseudo-state” where CC expansion is extended to a finite-range of states. There are methods to consider two electrons leave the target after the collision: ‘time-dependent close-coupling’ (TDCC) method and ‘exterior complex scaling’ (ECS) method. The CCC, RMPS, TDCC, ECS methods have been successfully used for collisions with intermediate energy ranges. For high energy regime, perturbative methods such as the

distorted-wave Born approximation (DWBA) or plane-wave Born approximation (PWBA) are applicable. For heavy targets relativistic approaches are necessary as the projectile energy may become relativistic near the nucleus.

It is noted that semi-empirical methods of ‘binary encounter f-scaling’ (BEf) and ‘binary encounter Bethe’ (BEB) are widely used in applications. The only way to access the uncertainties of these methods is by comparing with experimental data which are scarcely available.

While many of UQ issues are similar to electron-atom collisions, those of electron-molecule collisions should consider processes of not only an electronic excitation but also excitation of nuclear motion. The other difficulty is that there is no general method to solve for all the processes in a unified and consistent manner because of the nuclear motion. Generally, calculations of electron excitation or ionization processes use the fixed nuclei approximation but vibrational, rotational or dissociation processes include nuclear motion inherently. For vibrational collisions with molecular ions, the frame approach coupled with multi-channel quantum defect theory (MQDT) is reasonable. Rotational motion can be treated by a frame transformation approach (a transformation from the body-fixed frame to the laboratory frame by simple angular momentum recoupling), which was shown to work well compared to full CC treatments. The processes with nuclear motion such as rotational and vibrational excitation, dissociation processes are dominant in low energy regime and the cross-sections are very sensitive to the interatomic potential curves, which is a major source of uncertainties.

Similarly to the FPA approach, electron-molecule collision models are varied to provide uncertainty information. The simplest collision model is the static exchange (SE) model of electron collisions interacting with a target described by a HF wave function. The next sophisticated model is the static exchange plus polarization (SEP) model to include many more virtual orbitals to include polarization effects.

For small molecules vibrational wave functions is usually good and the uncertainty is more associated with the quality of the geometry fixed scattering matrix though for larger polyatomic ions, the poor wave functions contributes to uncertainties of the cross-sections significantly. The scattering matrix can be computed using electron scattering codes such as R-matrix, complex Kohn or variational Schwinger methods.

4. Charge Transfer in Ion-Atom And Ion-Molecule Collisions

As a positively charged ion collides with an atomic or a molecular target, an electron can be transferred between two systems. The full Schrödinger equation can’t be solved accurately except for the simplest case between nuclei and electron and therefore approximations should be made to

solve the equation depending on the situations. The de Broglie wavelength of a projectile relative to the length scale of electronic processes is important to determine the types of approximations in low energy collisions. For intermediate energy or high energy collisions, the relative projectile-target speed relative to the orbital speeds of the active electrons.

Following the discussion in Ref. [6], for low to intermediate energies, CC expansion methods have been used while the basis-set convergence and the model uncertainties are major sources of uncertainties. One can eliminate model uncertainties in the very low energy regime where a fully quantum mechanical description is used and the electron transfer is considered the real and avoided crossings of potential energy curves of the molecular system of projectile and target. This perturbed stationary state (PSS) approach has limitation and should be corrected with electron translation factors. Alternatively the hyperspherical close coupling (HS-CC) approach is used by writing Schrödinger equations on hyperspherical coordinates. For few electron systems, a quantum chemistry method of the quantum mechanical molecular-orbital close-coupling (QMOCC) calculations is often used as more general approach.

For high collision energies above 1 keV/amu, quantum-mechanical approach is very challenging and a semiclassical approximation is often used as the projectile de Broglie wavelength is small. The full scattering problem is converted to a time dependent Schrödinger equation for the electron motion in the field of classically moving nuclei where the trajectories are determined by the nonadiabatic coupling of the electronic and nuclear motion. At higher energies above a few keV/amu, the trajectories are assumed to be straight.

As direct target ionization becomes important for intermediate energy ranges, CC techniques should include converged sets of positive energy pseudo-states and two-center atomic orbital AOCC method or two-center basis generator method TC-BGM method are widely used. It is noted that there are cases where too large basis sets degraded the results in two-center methods. A direct numerical approach such as TDSE where the time-evolution operator is applied to electron wave function on a grid in a small time step provides reasonable results. It provides the electron density distribution in the continuum in addition to charge transfer cross-sections. In the nonrelativistic high energy regime, perturbative methods such as distorted-wave methods are used for charge transfer problem.

In the case of multiple electron transfer, approximations are made and the level of the semiclassical TDSE method is available. Many electron Hamiltonian is replaced by a sum of effective one-electron Hamiltonians so called independent electron model (IEM). Semi-empirical or classical methods such as two-state quantum mechanical models or the classical over-barrier model, classical trajectory Monte Carlo method (CTMC) are widely used

even in the low energy regime where quantum effects are important.

Finally, it is important to note that the electron transfer cross-sections are not directly measured but cross-sections deduced from post-collisional events are obtained. This implies that a modeling is required to obtain electron transfer and hence introduces uncertainties associated with experimental data, which makes the uncertainty quantification of calculated data by comparing with experiments much more difficult.

5. Particle-surface and plasma-material interactions

The particle-surface or plasma-material interaction (PSI, PMI) processes of primary interest for fusion are direct physical sputtering of surface material by high energy particle impact, chemical or chemically-assisted sputtering at lower impact energy (primarily affecting carbon-based surfaces), particle penetration and deposition in the surface, and finally migration and long-term retention of deposited hydrogen (and especially of the tritium isotope) in the material. Physical sputtering and fast particle penetration are relatively straightforward processes, not much dependent on the material microstructure, and for a long time the IAEA A&M Data Unit has provided relevant recommended data through the ALADDIN database [15], although without uncertainty estimates. Migration and long-term retention of hydrogen in fusion wall material is a much more complicated issue for simulations as it depends sensitively on atomistic-scale defects in the material that can act as trapping sites for the hydrogen.

There is a wide range of computational methods being used to simulate PSI and PMI, from single particle kinetic simulations based on the binary collision approximation (BCA) as embodied in the TRIM/SRIM and family of codes, via many-particle molecular dynamics based on force fields, to quantum-mechanical calculations of trapping energies and migration barriers. In all these fields the science of uncertainty quantification is severely underdeveloped. It is common to find uncertainty estimates for fundamental elementary calculations (for example a density-functional theory-based calculation of trapping energies or migration barriers), it is also common to find pointwise assessments of uncertainties in a force field, but it would be extremely rare to find those fundamental uncertainties propagated through a calculation to provide finally estimated uncertainties in calculated erosion, deposition and migration properties relevant to plasma-wall interaction in a fusion device. We do not know of systematic calculations of that nature that include uncertainty estimates.

In spite of the wide range of computational methods it looks possible to single out one concern that is most in need of attention for the purpose of uncertainty assessment of calculations of particle-surface and plasma-material interactions. We think that that central issue is the effective representation of uncertainties in a force field or interaction

potential and the propagation of these uncertainties through a molecular dynamics calculation. Other uncertainties appear to be either less important or more easily controlled. Thus, uncertainties in a BCA model can be assessed by selected comparisons with more rigorous molecular dynamics calculations, uncertainties in the pointwise energetics on the energy landscape (defects, binding energies, migration barriers) can be assessed through different electronic structure calculations, uncertainties due to the neglect of electronic excitations (if they are indeed neglected) are important only in the high-energy stage of a fast-particle impact, uncertainties due to neglect of quantum effects on the nuclear motion (if they are indeed neglected) are important only for cryogenic materials, and uncertainties due to the sampling in an MD calculation are understood and can be controlled even if this is difficult for the case of rare events. Without dismissing investigations into all these sources of uncertainty we still judge that for most calculations of particle-surface and plasma-material interaction for fusion devices the key source of unquantified uncertainty is the propagation of uncertainties in the force field or interaction potential through a molecular dynamics calculation.

Finally that concern of the propagation of uncertainties in the force field through a molecular dynamics calculation involves first the question of how to represent the uncertainty in the force field in an effective way to permit sampling from different force fields and second the question of how to condense the data from many molecular dynamics simulations for the many sampled force fields to obtain at the same time an estimate for the quantities of interest (trapping rates, transport coefficients) and an estimate for the uncertainties in those quantities. And finally, it will not be satisfactory to say that one just needs to take the basic MD calculation including its sampling process for a single force field and replicate it one thousand times for different force fields to estimate an uncertainty. The challenge is to develop an approach that will be used in practical work to obtain an uncertainty estimate alongside the primary quantities of interest without a massive increase in computational effort.

IV. CONCLUSIONS

The status of uncertainty quantification for atomic, molecular and nuclear data is reviewed. At the present state of theoretical understanding and computational capabilities the development of fundamental data for nuclear structure and reactions (energy levels, lifetimes, branching ratios and cross sections) involves the use of nuclear models tied down by measurements. Systematic Bayesian approaches employing Monte Carlo sampling with a prior distribution on the parameter space of the model and a posterior distribution based on available direct experimental data have been developed and are widely used to obtain

uncertainties in recommended cross sections, including uncertainties at energies for which measurements are not available and including a correlation structure among uncertainties at different energies or even for distinct processes.

Nothing like this is in routine use for atomic and molecular structure and collision data where the research is driven by the desire to obtain calculated data based entirely on the known fundamental equations; i.e., on the Schrödinger equation with Coulombic interaction and including known small correction terms. In practice, for spectroscopic properties of atoms and molecules uncertainties of calculated data are normally obtained by comparison with experiment, but for collision cross sections for atomic and molecular data the uncertainties often need to be quantified without any reference to experiment, and a genuinely satisfactory approach for this purely computational uncertainty quantification is still lacking. Largely following the earlier paper [6] we reviewed this research area. With respect to data for plasma-material interaction in fusion devices the situation lags behind even the state of atomic and molecular data; it is very difficult to obtain well characterized experiments when data are sensitive to material microstructure at the atomistic scale and this makes it essential to obtain uncertainty estimates strictly within a computational approach; we emphasized the central role of uncertainty quantification for molecular dynamics simulations starting with uncertainties in the underlying force field. Finally, as a pragmatic matter the aim for any kind of atomic, molecular, nuclear or materials data is to obtain reasonable estimates of the uncertainties with or without use of experimental data. We wish that this conference contribution will motivate other researchers in mathematics and computational science for nuclear science and engineering to contribute to the further development of objective mathematical procedures to estimate uncertainties of calculated data, particularly in the field of atomic, molecular and plasma-material interaction processes.

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