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Quantifying the Uncertainty on Ab-Initio Rate Coefficients by means of Bayesian Machine Learning

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ABSTRACT

Reaction rate coefficients are cornerstones in modeling hypersonic flows, as they quantify the rates at which the quantum states of the mixture components get populated, or depleted, as a result of collisional processes; they play a fundamental role in the identification of the energy-conversion mechanisms and, thus, in the final prediction of the heat fluxes experienced by the surfaces of hypersonic vehicles. Thanks to the exponential increase in computational power, in the last 15 years rapid progress has been made in computing state-to-state rate coefficients starting from the first principles of quantum chemistry, by taking advantage of Potential Energy Surfaces (PESs) for characterizing the interactions between atoms. However, the reaction rates obtained following such ab-initio procedure are heavily influenced by the choices that are made at the moment of deciding the geometric configurations at which the electronic SchrÃűdinger equation is solved, of selecting the techniques to use in order to obtain the electronic energies (i.e., electron correlation effects and atomic orbital basis set expansion), and of electing the functional form for fitting the points Fig. 1. Consequently, one of the priorities for the hypersonic community is the development of a systematic approach for assessing the impacts that such choices have on the flow-filed quantities of interest. We propose the construction of a non-deterministic PES, by extending in a stochastic manner the Permutation Invariant Polynomials Neural Networks proposed by Jiang and Guo. Bayesian Inference through the Automatic Differentiation Variational Inference algorithm by Kucukelbir *et al.* is applied in order to compute the posterior distributions of network's weights and biases. The stochastic PES, Fig. 2, is then sampled, and the gradients of the resulting surfaces are used as source terms of the Hamiltonian Equations, based on the Quasi Classical Trajectory method (QCT). By repeating these collisions for a number of initial atomic

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distances and velocities, it is finally possible to quantify the impact of the PES and trajectory dynamics uncertainties on the state-specific rate coefficients, Fig. 3.

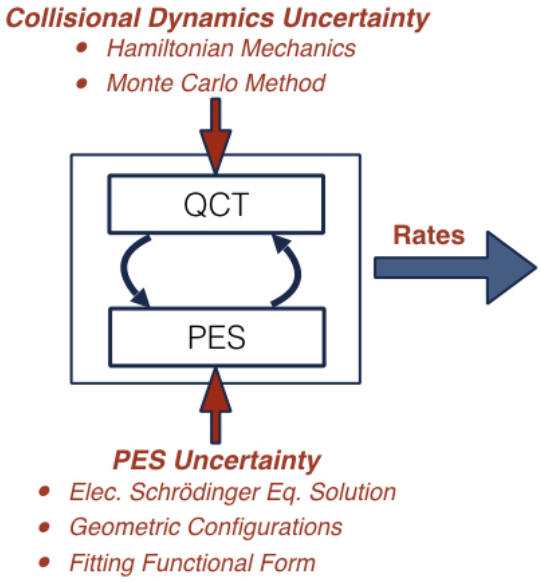

Figure 1: *Main sources of uncertainties in the ab-initio computation of rate coefficients.*

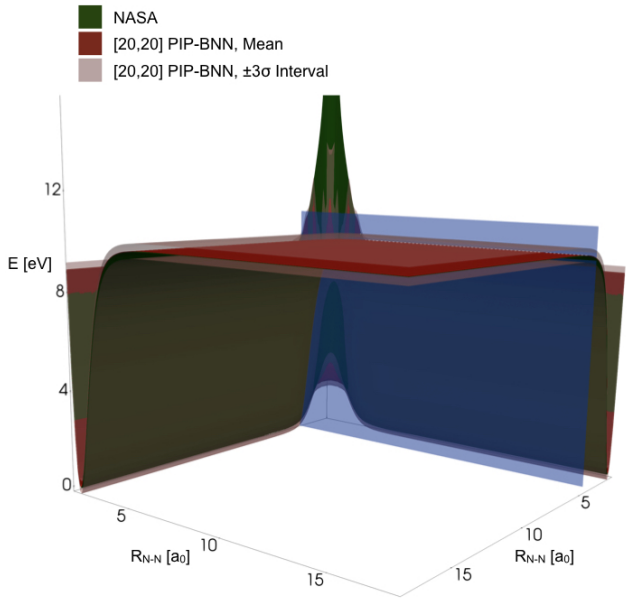

Figure 2: *Comparison between the Permutation Invariant Polynomial Neural Network (in red) and the N3 NASA Ames (in green) PESs.*

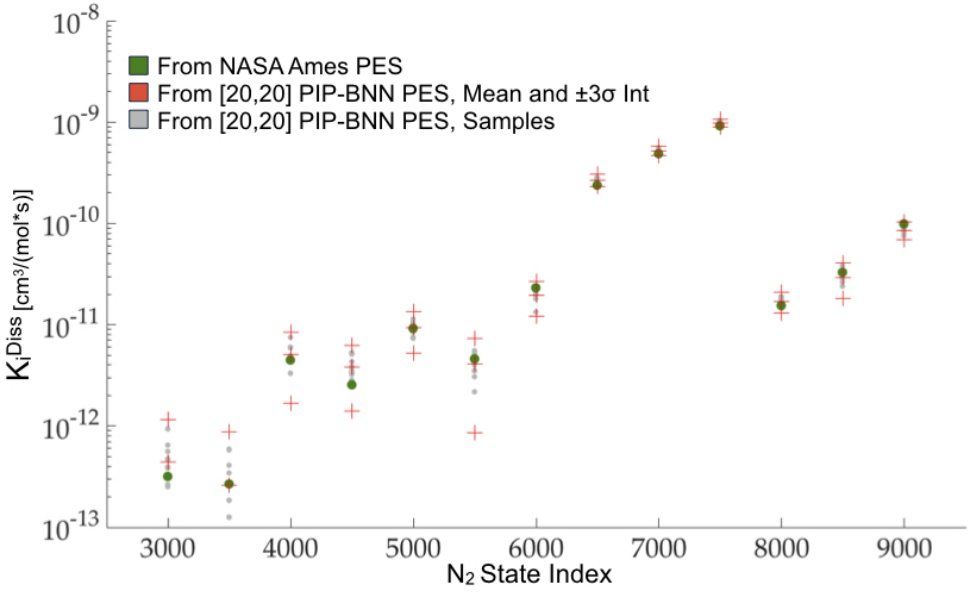

Figure 3: *Propagation of potential energy surface and collision dynamics uncertainties to some N_2 state-specific dissociation rates.*

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