Machine-learning the best potential surfaces for polyatomic molecules and the error bars for non-adiabatic atomic collisions

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We will present the application of kernel methods of machine learning to two problems in atomic and molecular physics.

Problem I:
The accuracy of quantum calculations of collision rates for atoms and molecules is limited by the inherent uncertainty of underlying potential energy surfaces. It is often difficult to assess the errors stemming from this uncertainty. This is particularly true for non-adiabatic collision processes that are determined by multiple interaction potentials. In the present work, we introduce a machine-learning technique based on Gaussian process regression for computing the error bars of collision rates corresponding to simultaneous variations of multiple adiabatic interaction potentials within the uncertainty of quantum chemistry calculations [1]. We show that the method can be used to obtain the sensitivity of the collision observables to individual electronic potentials [2]. This illustrates how machine learning can provide information on the mechanisms of electronic transitions.

Problem II:
Constructing accurate potential energy surfaces for polyatomic molecules is a major challenge. For a molecule with a large number of degrees of freedom, the difficulty arises both from the large number of ab initio computations required and from the uncertainty as to where in the configuration space to place the ab initio points in order to obtain the most accurate representation of the surface. We will show that both of these problems can be addressed with a machine-learning technique based on Gaussian processes. We will first show that Gaussian process regression yields a qualitatively good representation of the surface with a rather small number of ab initio points ($\sim$200 for a 6D surface) [3]. We will then illustrate the application of Bayesian optimization with Gaussian processes as an efficient method for sampling the configuration space of polyatomic molecules. Bayesian optimization is based on an iterative procedure, where, at each iteration, the surface is constructed by Gaussian process regression and a small set of ab initio points is added in the part of space determined by maximizing the so-called acquistion function. The acquisition function quantifies the improvement of the accuracy of the potential energy surface thus obtained.

References

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