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Development of new density functionals and new methods for analysis of convergence of ab initio molecular dynamics simulations.

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Abstract

We describe a method, that we call data projection onto parameter space (DPPS), to optimize an energy functional of the electron density, so that it reproduces a dataset of experimental magnitudes. Our scheme, based on Bayes theorem, constrains the optimized functional not to depart unphysically from existing it ab initio functionals. The resulting functional maximizes the probability of being the ``correct'' parametrization of a given functional form, in the sense of Bayes theory. The application of DPPS to water sheds new light on why density functional theory has performed rather poorly for liquid water, on what improvements are needed, and on the intrinsic limitations of the generalized gradient approximation to electron exchange and correlation. Finally, we present tests of our water-optimized functional, that we call vdW-DF-w, showing that it performs very well for a variety of condensed water systems.

In a second part, we present a method to evaluate the convergence of different parameters in ab initio molecular dynamics (AIMD). Monitoring convergence, as a function of basis set size and other precision parameters, is a necessary but costly process. It generally involves a new simulation for each parameter value, whose comparison is hindered by the statistical errors of each simulation. We describe an efficient method to monitor convergence, using simple ideas from perturbation theory and thermodynamic integration. It involves comparing results with different parameters, for a moderate set of snapshots taken from a single simulation. We show how the convergence of many thermodynamic and structural properties can be accurately assessed as a function of typical precision parameters of AIMD simulations. While the changes of convergence tests are generally small, we show that our technique is useful to address even much larger changes, like those involved in comparing different electron density functionals.

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