How to Ensure the Accuracy of Polarizable Force Fields?

***T. Verstraelen*[a]**
[a]Center for Molecular Modeling (CMM), Ghent University, 9000 Gent, Belgium;
e-mail: Toon.Verstraelen@UGent.be

Abstract

Traditionally, force fields are computationally efficient models for intra- and intermolecular interactions. The potential energy is approximated as a sum of two-, three- and four-body terms. In many force-field simulations, host-guest interactions determine the relevant results, e.g. the spatial distribution of guest molecules in a porous material [1], or the binding free energy of a ligand in an enzyme [2]. Because the accuracy of non-covalent interactions is so critical, one started incorporating explicit treatments of electronic polarization in force fields in the early nineties [3]. These so-called polarizable force fields (PFFs) seek to improve accuracy with a modest computational cost. The mutual polarization of two compounds leads to an additional attractive force that is unattainable with few-body terms. Despite intensive research, the development of a PFF is still a very complex and labor-intensive procedure [4]: parameters are calibrated empirically with diverse sets of reference data, including hydration energies, NMR data and ab initio data.

To facilitate the development of accurate PFFs, we propose to eliminate the empirical factors and to construct these models rigorously from an ab initio description of the electronic linear response. To this end, we recently derived the ACKS2 model from Kohn-Sham Density Functional Theory (KS-DFT) and showed that conventional PFFs are lacking important non-local contributions due to the electronic kinetic energy [5]. In this paper, we generalize the theoretical foundations of the ACKS2 model, building on other theories than KS-DFT and including atomic multipoles to arbitrary order. We validate our approach numerically, showing that accurate ab initio PFFs can indeed be constructed without the empirical calibration of parameters.

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