Using Density Functional Theory for estimating force field parameters

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Ab initio quantum mechanical calculations based on density functional theory (DFT) are nowadays used as the method of choice to model the potential energy surface (PES) of a large variety of systems. The main advantages of DFT models are their accuracy and their transferability to chemically very diverse systems. Unfortunately, despite its computational interesting features, DFT is still too expensive for larger systems with dimensions in the order of magnitude of several nanometers. This is especially true when one wants to derive macroscopic properties with Monte Carlo and Molecular dynamics simulations

Force fields provide an alternative PES model to overcome the computational limitations of the DFT approach. In force-field simulations the exact electronic structure is neglected. Instead, the PES is approximated with a sum of a priori determined analytical functions, containing unknown parameters, that describe the covalent bonds, bends, dihedrals and non-bonding contributions such as electrostatic and van der Waals interactions. To estimate the unknown parameters, one can either use experimental data or quantum mechanical calculations. In literature, some recent works have shown that it is possible to derive the force-field parameters from DFT calculations [1, 2]. However, one major drawback still is the inability to derive dispersion parameters from DFT calculations. Furthermore, the existing schemes to calculate atomic charges from the molecular electron density are rather ambiguous.

In this work, we derive a force field to describe the PES of the metal-organic framework MIL-53(Al) - an example of a larger nanometer scaled system - by using DFT calculations on the periodic structure and two representative clusters. Using a variety of partitioning schemes on the molecular electron density, we calculated atomic partial charges, dispersion coefficients and atomic radii to describe the non-bonding interactions. The influence of periodic versus cluster-based calculations was investigated and the results were compared with literature. In a second step, covalent parameters were estimated by fitting the force-field forces and hessian in the equilibrium to their DFT counterparts. Finally, the force fields ability of reproducing the DFT PES was validated by performing geometry optimizations and an additional PES scan using the force field and comparing the results with DFT calculations. This study has shown that DFT may be used to estimate force field parameters provided that also complementary models are used to deduce appropriate parameters for the non-bonding interactions.

References:

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[2] Marek S, Sauer J *Faraday Discuss.*, 106 (1997) 41-62.