

Non-covalent force field expressed in terms of spherical density functions

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Modeling non-covalent interactions in atomistic simulations, e.g. of biomolecules or porous materials, remains a challenging task. The traditional force-field approach with Lennard-Jones potentials and point-charges relies on a large number of empirically adjusted parameters, which are assumed to be transferable over a wide range of systems. However, when such popular tables of Lennard Jones parameters are validated against high-level ab initio calculations, one observes unacceptably large errors. This has stimulated the development of ab initio force fields for non-covalent interactions, in which force field parameters are adjusted on a case-by-case basis to reproduce SAPT or CCSD(T) reference data.

In this talk, I will present a new type ab initio non-covalent force field, the Monomer Electron Density Force Field (MEDFF), which only contains three global adjustable interaction parameters. All remaining information needed by the model is derived from the unperturbed electron densities of interacting fragments, which needs to be computed just once prior to the force-field simulation. This strategy eliminates the risk of overfitting a large number of adjustable parameters. Despite its limited complexity, MEDFF performs remarkably well for dispersion-dominated interactions.

MEDFF employs approximate electron densities, sums of spherical atoms, for the sake of computational efficiency and compatibility with existing models and software implementations. The spherical atoms are expressed as a sum of spherical Slater density functions, such that all integrals in MEDFF can be computed analytically at a typical force-field cost. The expansion in Slater functions is fitted to a reference electron density of a molecular fragment with the Minimal Basis Iterative Stockholder (MBIS) method. As opposed to traditional density fitting, MBIS uses the Kullback-Leibler divergence as a loss function and it can therefore also be interpreted as a variant of the Hirshfeld partitioning method. The strengths and weaknesses of MBIS as a populations analysis method will also be discussed.