Importance of the electronic kinetic energy in polarizable force fields

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Traditionally, a polarizable force field (PFF) is a classical model for the local electronic linear response of molecules and solids. The recent extension of popular biomolecular force fields (AMBER, CHARMM, OPLS) with polarization terms is driven by the large demand for more reliable non-bonding interactions in molecular mechanics simulations. Also in other fields, PFFs are used to improve the accuracy of non-covalent force fields, e.g. for the simulations of adsorption isotherms of small guest molecule in porous silica and metal-organic frameworks.

Nearly all PFFs attach an inducible dipole to each atom, either in the form of a Drude oscillator or as an inducible point dipole. Some PFFs also include variable charges (e.g. CPE) or even use them exclusively (EEM, Qeq, CHEQ, FlucQ or FQ). In any case, these PFFs always use classical electrostatic interactions between charges and/or dipoles at different sites.

It is generally accepted that atomic partial charges are the consequence of differences in intrinsic chemical potential and an external field acting on the molecule. It should therefore be surprising that most PFFs only use atomic inducible dipoles and thus skip the first term in the atomic multipole expansion. However, when variable atomic charges are included in a PFF, the model obtains two major undesirable properties: (i) the dipole polarizability scales cubically with system size (unlike the linear scaling one expects for dielectric systems) and (ii) molecules dissociate into fragments with fractional partial charges. We recently proposed a new type of PFF, atom-condensed Kohn-Sham DFT approximation to second order (ACKS2), that overcomes both limitations. Compared to a traditional PFF, ACKS2 introduces a new energy term for the electronic kinetic energy. This extension implies an extra non-classical interaction for charges and dipoles at different sites. Additional advantages of the ACKS2 model include the direct derivation (not calibration) of PFF parameters from a Kohn-Sham wavefunction and a modest increase in computational cost compared to a conventional PFF.

In this work, we'll briefly review the theory of the ACKS2 model and discuss the pragmatic aspects of obtaining transferable and accurate ACKS2 parameters for a set of organic molecules.

Keywords

Polarizable force fields, transferability versus accuracy, linear response, Kohn-Sham density functional theory, charge-transfer polarization