ACKS2: Atom-Condensed Kohn-Sham DFT approximated to second order

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The Electronegativity Equalization Method (EEM) proposed by Mortier in 1986 is the simplest yet effective model to understand and compute the molecular electron distribution [1]. The EEM approximates the DFT electronic energy as a quadratic expression of the atomic populations, in which conceptual DFT quantities (the atomic electronegativity and hardness) appear as model parameters. Over the past 20 years, several extensions of the EEM were proposed, with more realistic inter-atomic Coulomb interactions (e.g. Qeq [2]) or with atomic inducible dipoles (e.g. CPE [3]). Computational assessments have clearly demonstrated that such models can accurately predict atomic partial charges of small molecules.

Two important weaknesses of the EEM were extensively discussed in the literature. First, the EEM predicts a cubic scaling of the dipole polarizability with system size. It is therefore not suitable as a polarizable force-field for extended dielectric systems, which should exhibit a linear scaling [4,5]. Second, upon dissociation of a molecule, the EEM predicts non-integer charges for the fragments [6], which undermines the application of EEM in reactive potentials such as ReaxFF. Even though the EEM is computationally feasible for extended molecular systems, these two weaknesses limit the applicability to small isolated molecules. Many ad hoc solutions were proposed based on empirical or physical arguments. Only recently, a fundamental extension of the EEM was presented, i.e. the ACKS2 model, in which both issues are resolved [7].

In analogy with the EEM, ACKS2 is derived from DFT but now the Kohn-Sham kinetic energy is explicitly taken into account via a Legendre transform. Because ACKS2 surmounts the two aforementioned weaknesses with a small extra computational cost, it provides a solid foundation for future polarizable and reactive force fields. An additional advantage is that all ACKS2 parameters are defined as atoms-in-molecules expectation values, such that the tedious statistical calibration of model parameters can be avoided. The impact of this work goes beyond the development of polarizable force fields. Our computational assessments reveal that one cannot simply model the molecular polarizability with a set of interacting inducible atomic dipoles, while this is often assumed in the development dispersion corrections for DFT. Inter-atomic charge transfer always has a significant contribution and it is largely responsible for the anistropy of the dipole polarizability tensor.

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