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

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Sanderson's principle of electronegativity equalization states that, upon formation of a molecule, electrons flow until all electronegativities are equalized.[1] Essentially the same principle is found in density functional theory (DFT), stating that the electronic ground state has a constant chemical potential. Starting from basic DFT equations, Mortier et al. derived the electronegativity equalization method (EEM),[2] providing an elegant mathematical reformulation of Sanderson's principle. The molecular electronic energy is approximated to second order in terms of atomic populations. Minimization of this energy with a total charge constraint leads to a set of linear electronegativity equations, predicting fairly accurate atomic partial charges.

Over the past two decades, the EEM was thoroughly tested for a variety of chemical systems.[3,4] Several extensions of the model were proposed, such as more realistic interatomic potentials[5] or the inclusion of p-type density basis functions.[6] Applications can be found in molecular mechanics models[7] and QSAR.[8] Recently, it became clear that the EEM also has some fundamental limitations. Firstly, the EEM predicts that the dipole polarizability of a chain molecule grows cubically with the chain length, while one expects a linear trend in the macroscopic limit for dielectric molecules.[9] Secondly, one obtains fractional charges when a molecule dissociates, while one expects integer-charged fragments. These errors limit the applicability of the EEM to isolated molecules where an incorrect polarizability is acceptable. For other systems, one must introduce ad-hoc constraints to limit the impact of both errors.[10]

In this paper, we propose a successor for the EEM: "Atom-Condensed Kohn-Sham DFT approximated to second order" (ACKS2). Relying on principles from constrained DFT[11] and the Legendre transform approach to the Kohn-Sham kinetic energy,[12] a more general approximation for the electronic energy in terms of atomic populations is derived from Kohn-Sham DFT. This new form can exhibit both metallic and dielectric limits for the dipole polarizability (in analogy with the split-charge equilibration[9,13]) and enables a correct dissociation limit for the atomic partial charges. A minimization of the ACKS2 energy with a total charge constraint leads to a set of linear equations that only have a marginal computational overhead compared to the EEM equations. We expect that this new model will become an essential component of future polarizable and reactive force fields.

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