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

Toon Verstraelen[†], Paul Ayers[‡], Veronique van Speybroeck[†] and Michel Waroquier[†]

[†]Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Ghent, Belgium; (Member of the QCMM Ghent-Brussels Alliance Group),
[‡]Department of Chemistry, McMaster University, Hamilton, Ontario, Canada, L8S 4M1

E-mail: Toon.Verstraelen@UGent.be

Sanderson's principle of electronegativity equalization states that, upon formation of a molecule, electrons flow until all electronegativities are equalized. 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), 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. Several extensions of the model were proposed, such as more realistic interatomic potentials or the inclusion of p-type density basis functions. Applications can be found in molecular mechanics models and QSAR. Recently, it became clear that the EEM also has some fundamental limitations. First, 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. Second, one obtains fractional charges when a molecule dissociates, while one expects integer-charged fragments. These errors limit the applicability of the EEM to small isolated molecules where an incorrect polarizability is acceptable. For other systems, one must introduce ad-hoc constraints to limit the impact of both errors.

In this poster, we propose a successor for the EEM: "Atom-Condensed Kohn-Sham DFT approximated to second order" (ACKS2). Relying on principles from constrained DFT and the Legendre transform approach to the Kohn-Sham kinetic energy, 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) 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.