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A new DFT approach to polarizable force-fields

T. Verstraelen[1]

[1] *Center for Molecular Modeling, Ghent University, Belgium, 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 [1]. The molecular electronic energy is approximated to second order in terms of atomic charges. Minimization of this energy with a total charge constraint leads to a set of linear electronegativity equations, predicting fairly accurate atomic partial charges. In principle, EEM could also be used to describe electronic linear response properties such as the molecular dipole polarizability or the dielectric constant of a crystal.

A polarizable force-field is essentially a generalization of the EEM, often including inducible atomic dipoles (and quadrupoles). It is even very common to fix the atomic charges and to describe the linear response properties with only the inducible dipoles. At first sight, it is counter-intuitive to neglect the response contributions from the atomic monopoles and to work only with the contributions from higher multipoles. However, this tendency in the literature can be explained on the basis of the fundamental limitations of EEM, which were only revealed recently. 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 [2]. Furthermore, EEM predicts a non-integer charge transfer between different molecules, even when they are well separated. These problems limit the applicability of the EEM to small isolated molecules where an incorrect polarizability is acceptable.

In this talk, we propose a successor for the EEM: "Atom-Condensed Kohn-Sham DFT approximated to second order" (ACKS2) [3]. Relying on principles from constrained DFT and the Legendre transform of 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 [4]) 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. Computational benchmarks of the ACKS2 model show that the good prediction of the anisotropy of the dipole polarizability is one of the particular strengths of the model.

References

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