

**43 - Charge transfer in polarizable force fields: Importance of the electronic kinetic energy**

**Toon Verstraelen**<sup>1</sup>, [Toon.Verstraelen@UGent.be](mailto:Toon.Verstraelen@UGent.be), Paul W Ayers<sup>2</sup>, Veronique Van Speybroeck<sup>1</sup>, Michel Waroquier<sup>1</sup>. (1) Center for Molecular Modeling, Ghent University, Zwijnaarde, Oost-Vlaanderen B9052, Belgium, (2) Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Molecular mechanics or force-field models are used in diverse domains, e.g. simulation of enzymes, material science, etc. Due to the empirical approximations in a force field, the accuracy of non-covalent interactions is limited. A polarizable force field (PFF) explicitly includes electronic polarization effects to improve the accuracy of non-covalent interactions. A PFF is essentially a second order approximation of the molecular electronic energy with a minimal density basis set that accounts for atomic charges and dipoles. It is common to fix the atomic charges and to describe linear response properties with inducible dipoles only. Without this restriction, a conventional PFF exhibits several undesirable artifacts. For example, when charges are allowed to fluctuate, one observes 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. Furthermore, variable charges also lead to a fractional charge transfer for well-separated molecules. In order to account properly for atomic charge fluctuations, we propose a new type of polarizable force field: "Atom-Condensed Kohn-Sham DFT approximated to second order" (ACKS2). Compared to conventional PFFs, ACKS2 contains a new energy term based on a Legendre transform of the Kohn-Sham kinetic energy. ACKS2 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. 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.

**Sunday, March 16, 2014 04:15 PM**

[Molecular Mechanics \(01:30 PM - 05:15 PM\)](#)

**Location: Omni Dallas Hotel**

**Room: Trinity 5**

\*ACS does not own copyrights to the individual abstracts. For permission, please contact the author(s) of the abstract.

[Close Window](#)