Using the Charge Response Kernel with the Minimal Basis Iterative Stockholder Definition of Atomic Charges to Model Polarization Effects in Force Fields

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In this work, we look at the modelling of polarization effects in force fields by using atomic charges. We expand the framework of the Bond Capacity (BC) model[1], which accounts for the polarization in the force field energy functions by allowing charge-flow between pairs of atoms. To determine the BC-parameters a linear response formalism like the Charge Response Kernel (CRK), originally proposed by Morita and Kato[2], is introduced. The CRK can be viewed as the derivative of atomic charges with respect to changes in the potential, and thus quantifies the charge-flow capability between atoms. The original formalism uses atomic charges defined by fitting to the electrostatic potential (ESP), but this is known to be numerically problematic. We aim to calculate the CRK with the Minimal Basis Iterative Stockholder (MBIS) definition of atoms in molecules[3], which removes the problems of fitting to the ESP.

Preliminary tests by finite field calculations show promising results for the BC-parameters, with 1,3-pairs being of redundant size for non-conjugated systems and inclusion of up to 1,4-pairs being able to describe conjugated systems well. These calculations also show an improved transferability between similar atoms at a small cost in accuracy compared to ESP, which is promising with a force fields parametrization in mind.

References

1. *Poier, P.; Jensen, F. "Describing molecular polarizability by a bond capacity model." Journal of chemical theory and computation 15.5 (2019): 3093-3107.*
2. *Morita, A.; Kato, S. "Ab initio molecular orbital theory on intramolecular charge polarization: effect of hydrogen abstraction on the charge sensitivity of aromatic and nonaromatic species." Journal of the American Chemical Society 119.17 (1997): 4021-4032.*
3. *Verstraelen, T.; et al. "Minimal basis iterative stockholder: atoms in molecules for force-field development." Journal of Chemical Theory and Computation 12.8 (2016): 3894-3912.*