Modeling Charge-Transfer Interactions With The ACKS2 Model

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The electronegativity equalization method (EEM) is one of the first models to approximate the electronic energy of a molecule as a quadratic function of the atomic partial charges. [1] (Models like QEq, FlucQ, etc. are very similar to EEM but were developed later.) In principle, EEM can, with only a few simple atomic parameters, make coarse estimates interaction energies between molecules, accounting for changes in partial charges they induce onto each other. For this reason, it is used as a component in many force fields, e.g. in ReaxFF. Unfortunately, EEM allows spurious long-range (through-space) charge transfer, which has two well-known manifestations: (i) a molecular dimer may exchange charge in the dissociation limit and (ii) the polarizability of an extended system scales cubicly with system size. Several corrections were proposed to mitigate these weaknesses, e.g. by imposing constraints on the total charge of each molecule in a simulation. [2]

We recently proposed the Atom-Condensed Kohn-Sham approximation to second order (ACKS2), which is an EEM-like model that properly accounts for the electronic kinetic energy. [3] Later, the model was generalized: it can be derived from any variational electronic structure theory, not just KS-DFT, and it can describe fluctuating atomic multipoles, not just atomic charges. [4] The ACKS2 model has the following conceptual benefits:

1. Spurious long-range charge transfer, as in EEM, is not observed.
2. The equations can be seen as an approximate linear response theory of an underlying electronic structure theory. In the limit of a complete basis set for density and potential fluctuations, the linear response of the underlying theory is reproduced exactly.
3. All parameters in the ACKS2 model, for a given molecular geometry, can be computed as atoms-in-molecules expectation values. This reduces issues with the statistical calibration of polarizable force-field parameters, because good estimates of the parameters can be computed directly.

In this talk, I will review the basic theory and discuss our recent efforts to obtain practically useful parameterizations of the ACKS2 model. In general, the challenge is to find a good trade-off between the robustness of the parameters, i.e. a reasonable geometry dependence, and the overall accuracy of the model, i.e. reproduction of electrostatic and induction interaction energies.

References

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