Can we derive many-body non-additive polarization energies from 1-body properties and 2-body energies only?

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Force-fields are normally fitted to a range of data, which could be experimental or theoretical, or a mixture of both. As a rule, many-body intermolecular interaction models are fitted to a range of energies computed on dimers, trimers and often even larger clusters of the interacting molecules. This is done so as to get a good representation of the many-body interactions in the system, but while it is possible to make such extensive computations on small systems like water, it is not generally feasible on larger systems. So we raise the question: Can we derive the many-body polarization energies from molecular properties and a dimer energy evaluations only?

Using very recent work on water models [1] we demonstrate that this is indeed possible. Central to this scheme are the distributed molecular multipoles computed using the basis-space implementation of the iterated stockholder atoms (BS-ISA) algorithm [2], the distributed molecular polarizabilities computed using the ISA-Pol algorithm [3], and charge-delocalization energies defined using regularized-SAPT(DFT) [4]. With these ISA-based molecular properties and a limited number of SAPT(DFT) and regularized-SAPT(DFT) interaction energies computed on dimers only, we can now construct accurate many-body interaction models that correctly describe many-body polarization effects. Using a series of water models of varying complexity we demonstrate how these DIFF (derived intermolecular force fields) models are very close to optimal and have a remarkable predictive power for both the energerics and geometries of large water clusters.

All of the techniques described in this talk are available in the CamCASP code [5] and more information can be found on the CamCASP wiki.

[1] "Many-body non-additive polarization energies for water clusters from first principles polarization models", Rory A. J. Gilmore, Martin T. Dove, and Alston J. Misquitta (in preparation).

[2] BS-ISA: "Distributed Multipoles from a Robust Basis-Space Implementation of the Iterated Stockholder Atoms Procedure", A. J. Misquitta and A. J. Stone and F. Fazeli, J. Chem. Theory Comput. **10**, 5405 (2014).

[3] ISA-Pol: "ISA-Pol: Distributed Polarizabilities and Dispersion Models from a Basis-Space Implementation of the Iterated Stockholder Atoms Procedure", Theor Chem Acc (2018) 137: 153. https://doi.org/10.1007/s00214-018-2371-4.

[4] Reg-SAPT(DFT): "Charge-transfer from Regularized Symmetry-Adapted Perturbation Theory", Alston J Misquitta, J. Chem. Theory Comput. **9**, 5313 (2013).

[5] CamCASP: Cambridge package for Calculation of Anisotropic Site Properties, Alston J Misquitta and Anthony J Stone, `https://app.ph.qmul.ac.uk/wiki/ajm:camcasp:start`