

New developements in three-body non-additive intermolecular interactions

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Non-additive many-body interaction energies are increasingly important for large molecular clusters or condensed phases, but due to the challenges in their calculations, these contributions are frequently neglected or treated implicitly by lumping these terms into pair contributions. Density Functional Theory (DFT) is a frequently applied method for studying intermolecular interactions. After introducing the empirical correction, the resulting DFT-D approach achieves very good accuracy, sufficient for many applications, and comes with a low computational cost. However, the DFT-D method falls short in modeling three-body non-additive interaction energies for many classes of molecular trimers. It turns out that this failure is caused by incorrect description of the non-dispersion parts in the short range, a problem which we present a detailed analysis in Ref. 1. Without robust methods such as DFT-D, three-body interaction energies need to be modeled with wavefunction-based methods. However, non-additive dispersion requires at least the third order of the perturbation theory, making the resulting calculations prohibitively expensive for even medium-sized systems. Non-additive dispersion calculated with symmetry-adapted perturbation theory [2] can be added on top of the second-order Møller-Plesset perturbation theory (MP2), resulting in an approach with a fifth-power scaling that achieves decent accuracy. We demonstrate that comparable or even superior accuracy can be obtained through empirical dispersion [1]. Additionally, we point out that local coupled-cluster-based methods, such as the DLPNO-CCSD(T) approach, lack the precision required to accurately model three-body non-additive effects. Finally, we demonstrate that very good accuracy can be achieved with a machine learning approach. We trained a neural network (NN) on accurate benchmark non-additive energies for water trimer using descriptors that combine supermolecular Hartree-Fock, non-additive exchange and induction contributions, and empirical non-additive dispersion. All these descriptors scale as the fourth power of the system's size or better. The resulting NN model achieves a root mean square deviation roughly half of that of the CCPOL3 [3] explicit water three-body potential.

References

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