The MP2 Basis Set Limit for Hydrogen Bonded Dimers[1]

Thomas Watson and Glênisson de Oliveira

Rhode Island College, Physical Sciences Department
600 Mt. Pleasant Ave., Providence, RI 02908

Weak interactions are very important and ubiquitous in nature. Hydrogen bonding in particular is crucial to biological structures, ranging from the double helix structure of DNA to proteins. In recent decades, computational approaches have been essential to our increased understanding of these interactions; however, these evaluations involve an intricate superposition of very small effects (hydrogen bonds, dispersion, intercloud penetration, exchange, and electrostatics) and obtaining very accurate and reliable results is costly and very demanding on the basis set. Accurate evaluations of weak interactions also require high-level computational methods, and the combination of high-level methods with very large basis sets, make studying these interactions very time consuming, sometimes impossible.

Because of the cost of accurate computations, there have been some very popular and well-established approaches designed to evaluate thermochemical properties of molecules, but similar methods are not available specifically for weakly bound systems. One of the key aspects of the aforementioned methods is an evaluation of the infinite basis set limit for the properties of interest. In this project, hydrogen bonded systems are studied, with each system having increasingly complex permanent moment tensors for the monomer (dipole, quadrupole, and octupole moments are consecutively present in the different molecules) – hydrogen fluoride, water, and ammonia dimers are used as test cases.

This work focuses on the use of sequential and consistent truncations of angular momenta from large basis sets. We also explore the use of counterpoise (CP) corrections; although CP corrections may not to be beneficial in all weak interactions, in the systems studied here, they greatly facilitate convergence, as uncorrected energies behave erratically. The infinite basis set limits obtained with truncated bases are shown to be very close to those obtained with complete correlation consistent bases, and for the test cases we examined the time savings can be a factor of 45 for MP2 calculations and as much as 165 for CCSD(T).

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