Efficiently and Accurately Reproducing CCSD(T) Optimized Structures and Vibrational Frequencies of Water Clusters with the N-body:Many-body QM:QM Method

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We present recent results from our N-body:Many-body QM:QM method for weakly bound clusters in which all 1-body through N-body interactions are computed with a high-level method, while the higher-order interactions ($> N$-body) are only obtained with a less demanding low-level method. If the chosen low-level method accurately reproduces the $> N$-body effects, then the errors remain small. The linear expression for the traditional many-body expansion gives the QM:QM energy and results in straightforward evaluation of geometrical derivative properties, including gradients and Hessians. Here, the procedure is employed to reproduce CCSD(T) optimized structures and harmonic vibrational frequencies of $(H_2O)_n$ clusters ($n = 3 - 6$). For all clusters, geometry optimizations performed with the 2-body:Many-body CCSD(T):MP2 method yield structures which are virtually identical to the CCSD(T) geometries. For vibrational frequency calculations, the 2-body:Many-body CCSD(T):MP2 frequencies typically differ from the corresponding CCSD(T) results by, at most, a few cm^{-1}. Maximum deviations between CCSD(T) and 3-body:Many-body CCSD(T):MP2 frequencies are typically only a few tenths of a cm^{-1}. These encouraging results are obtained at a fraction of the wall time of the canonical computation.