Efficient and Accurate Benchmark Optimized Structures and Vibrational Frequencies for Molecular Clusters with the N-body:Many-body QM:QM Method

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Abstract

Recent results will be presented from our N-body:Many-body QM:QM method for weakly bound clusters [1–5] 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. As with the ONIOM approach to integrated computations, a linear expression for the QM:QM energy is obtained, which leads to the straightforward evaluation of geometrical derivative properties, including gradients [6,7] and Hessians. Here, the procedure is employed to compute optimized structures and harmonic vibrational frequencies of small molecular clusters such as $(H_2O)_n$. The results are in near perfect agreement with those from canonical CCSD(T) computations. For all clusters, geometry optimizations performed with the 2-body:Many-body CCSD(T):MP2 method yield structures that 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}. Deviations between the CCSD(T) and CCSD(T):MP2 results can be systematically reduced by including higher-order interactions in the procedure. The 3-body:Many-body CCSD(T):MP2 approach, for example, provides vibrational frequencies within a few tenths of a cm^{-1} of the canonical CCSD(T) values. Furthermore, these accurate N-body:Many-body results can be obtained at a fraction of the wall time of the canonical computation with relatively modest computational resources..

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