EE-ONIOM-CT method to efficiently account for the missing interactions in ONIOM: Energies and Analytic Gradients

Vikrant Tripathy and Krishnan Raghavachari

Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

Abstract

Hybrid methods such as ONIOM are widely used for the study of local processes in large systems. However, the intrinsic need for system partition leads to less-than-desirable performance for many chemical processes. This is due to the missing interactions in the chemically important model region (i.e., active site) at the high-level theory. The missing interactions can be categorized into two classes, viz. charge transfer (i.e., charge reorganization between regions) and long-range electrostatic interactions. Our group has presented two entirely different methods to treat these deficiencies individually. ONIOM-CT and ONIOM-EE methods have been demonstrated to improve the performance of ONIOM by incorporating charge transfer and missing electrostatic interactions, respectively.

In general, the separation of missing interactions into two individual categories may not be sufficient to reach high accuracy. Thus, it is highly desirable to develop a method to correct both deficiencies simultaneously. Our new method aims at connecting the methods ONIOM-CT and ONIOM-EE for a more comprehensive treatment. We employ a stepwise procedure by first satisfying ONIOM-CT condition for charge balance before accounting for the electrostatic interactions from the rest of the system while keeping the model region density unchanged. We will demonstrate our method using embedding charges determined from a Mulliken population analysis. The analytic gradient expressions for this method have been derived and implemented. They require solving three sets of z-vector self-consistent equations, one for the full system at the low-level, and one each for the model system at low-level and high-level. Nevertheless, our implementation is efficient, and is assessed against full system calculations at high-level theory for sample problems involving proton transfer and other reactive processes.