Commentary

Fragmentation and Embedding Schemes in Accuracy of Quantum Chemical Methods

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DESCRIPTION

Practical application of advanced and most accurate electronic structure methods is still limited to quite small molecular systems containing at most a few atoms. When translated to a practical catalytic system, such an ensemble corresponds to only a fraction of a catalyst system that may not capture some crucial chemical features, resulting in very low model accuracy. Fragmentation schemes can extend applicability of standard quantum chemistry methods to larger molecular systems by dividing a system into smaller fragments. Computed results of each fragment are collected to evaluate energy of the complete system. Challenge that each fragmentation scheme has to address is how to provide an exact definition of no additive terms. Recent reviews on fragmentation schemes have extensively covered progress in this field. An important drawback of most fragmentation methods is that orbitals and, thus, wave function of system cannot be fully recovered. Consequently, this hinders their applicability to cases where understanding of electronic structure of a molecule is mandatory. So, applications of such approaches to transition metal catalysts are scarce. Analysis of excited states of an extended Zn-porphyrin chain, and incremental schemes that have been applied to transition metal complexes, such as $TiCp2Cl2$ and the Zn4-cluster, an important building unit of many metal-organic frameworks, are two intriguing examples that incorporate transition metals. In computational catalysis, methods based on subsystems treated at distinct levels of theory, such as hybrid QM/MM and ONIOM techniques, have become much more popular and have been effectively employed in several research on 3d transition metal catalysts. In both methods, full system is divided into two subsystems, "model system", which is treated with an accurate and more expensive method (WFT or DFT), and environment, which is treated with a lower level of theory, usually DFT or molecular mechanics (MM). In QM/MM, total energy is calculated as sum of three energy terms: model or primary subsystem (EQM), environment (EMM), and interactions (EQM-MM) between QM model system and MM environment system. ONIOM follows a different approach for calculation of total energy. It considers sum between energy of model with a higher

level of theory and energy of a full (real) system at a lower level and subtracts energy of model at a lower level. Both QM/MM and ONIOM can apply DFT and/or WFT as a higher level of theory to describe active site of a catalytic system, while they treat its environment with a lower level of theory. For that purpose, they have been applied in many studies on computational catalysis which have been covered in recent articles. Correct coupling between two subsystems is a computational difficulty that these approaches face. Because they do not rely on electrostatic parameters for coupling of two subsystems and can adjust the electronic structure of high-level subsystems to the charge distribution of the MM subsystem, electrostatically embedded fragment methods are considered more accurate than mechanically embedded fragment methods. Subsystem embedding methods can be thought of as an improved version of fragmentation methods, as they provide a precise attribute of the entire system. Frozen-density embedding (FDE) theory is a theoretical framework. Total density is represented as a sum of subsystem densities in subsystem DFT. Total density is calculated self-consistently by minimizing total energy with respect to subsystem densities, which simplifies electronic structure problems into subsystem problems. Similar approaches have been developed for extending subsystem Green's functions and subsystem density matrices. Evaluation of such new methodologies on transition metal complexes is scarce, but since this is a field of active research; applications on catalysis are expected in near future. Introducing a WFT method for (model) subsystem can circumvent that problem and provide an accurate description of local catalytic sites with correlated methods (WFT-in-DFT). Theoretical framework of a WFT approach employed in an embedding scheme was devised first, and then extended to molecules and materials by using an embedding potential derived using approximate functionals. A self-consistent reconstruction of embedding potential from a density partition is an extension to existing models. Since the WFT subsystem calculation has become the bottleneck of the WFT-in-DFT scheme, this step is no longer the most time-consuming. This technique can be used in conjunction with CASSCF and has the benefit of being able to handle covalent interactions between subsystems and the environment. Using

this WFT-in-DFT embedding technique, several researchers investigated cobalt diimine-dioxime catalysts for hydrogen evolution. The transition metal, its first coordination sphere, and atoms that are bridging the other atoms of first coordination sphere of Co were treated at CCSD(T) level, while resting of the complex with DFT [CCSD(T)-in-DFT scheme, (panels B and C)]. Potential energy curve along proton transfer coordinate obtained by DFT significantly deviates from that calculated with CCSD(T). The CCSD(T)-in-DFT embedding scheme can reproduce a pure CCSD(T) curve with significantly lower computational effort.

Similarly, a multilayer method was reported in which a CASSCF wave function with an internally contracted multireference coupled cluster (icMRCC) was embedded in local PNO-CASPT2. The icMRCC in this WFT-in-WFT method has limited active space, and subtractive multilayer ONIOM-type embedding is used between layers. Calculations on a nickel complex with 231 atoms and 4175 basis functions were done to demonstrate power of this method. icMRCC. Since multi-configurationally approaches may now be used at active site subsystem, WFT-in-DFT and WFT-in-WFT strategies are predicted to see more usage on large molecular catalysts in the future.