Perspective

Single-Reference Wave Function Theory and Ab Initio Molecular Dynamics for Catalytic Applications

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DESCRIPTION

To examine properties of isolated points, potential energy surface (PES), Conventional quantum chemical calculations (WFT or DFT) are commonly used in combination with geometry optimization methods to locate local minima and saddle points (transition states) at the 0K PES and compute their energies and all related properties derived from the solution of the electronic structure problem. This information can be related to the intrinsic reactivity of a catalytic system. In practice, however, the reactivity and catalytic performance are defined not only by the PES but also by the conditions at which the reactions are carried out, environmental effects associated with the medium where the reactions take place, and other "secondary" effects which are manifested by the condition-dependent free energies.

By combining electronic structure methods with classical mechanics approaches, the dynamic evolution of properties of solids, liquids, and interfaces at finite temperatures relevant to catalytic phenomena can be obtained, giving rise to the so-called Car-Parrinello molecular dynamics (CPMD) and ab initio molecular dynamics (AIMD) methods. The forces acquired from accurate, on-the-fly quantum chemical calculations are used to build trajectories from finite temperature molecular dynamics in AIMD. AIMD simulations can solve difficult problems that conventional force fields and quantum chemistry computations couldn't solve. Key aspects of a catalytic reaction can be examined from AIMD simulations, such as the role of the solvent medium and fast dynamical motion of light atoms. AIMD simulations on enzymatic reactions involving proton transfer promoted by transition metal-based active sites have been reported, such as the dismutation of superoxide radical anions, the catalase reaction (peroxide bond cleavage) from catalase/hydrogen peroxidases, hydrogen production from [FeFe]-hydrogenase, antibiotic hydrolysis by Metallo-β-lactamase enzymes, and Cu-mediated amyloid formation. Similar reactions involving proton transfer on biomimetic catalytic complexes and materials have been reported, such as hydrogenase model complexes, hydrogen production from water promoted by a hydrogenase-inspired catalyst [FeFe]/electrode complex [FeS2], or cobaloxime catalysts.

From the computational perspective, the AIMD and CPMD approach provides the possibility to directly probe entropic contributions to catalytic reactivity and acquire the conformational freedom of the reactive complexes that are necessary for accurate free energy calculations. Besides, the explicit consideration of solvent and the extended molecular structure of the catalyst system commonly employed with these methods substantially improve the model accuracy of the calculation and create an opportunity to study reaction channels that could not be otherwise probed with static approaches. However, these methods are highly demanding since they require long simulation times and sampling of many trajectories and can only be used to accurately evaluate selected reaction steps of the catalytic networks. Additional limitations to the applicability and the predictive power of the AIMD and CPMD methodologies arise from the classical description of the atomic trajectories and the adiabatic approximation to the potential energy surface (PES). These assumptions may have a detrimental effect on systems where quantum effects associated with the dynamics of light atoms are important or where the reactivity is contributed by the coupling of multiple Born-Oppenheimer PES.

Single-reference wave function theory for catalytic applications

For almost three decades, the gold standard of quantum chemistry has been coupled-cluster singles-and-doubles with perturbative triples (CCSD(T)), which can yield very precise results for a wide range of molecular applications. However, single-reference post-HF methods (including such extremely accurate CCSD(T) approaches) should be utilized with caution in transition metal chemistry and for researching bond breakage and formation for the reasons stated above. A highly correlated scheme, such as coupled-cluster theory, is ideal because it improves accuracy consistently by increasing the size of the basis set or the correlation level. This is also true for multiconfigurational approaches, although DFT does not have a straight consistent rise in accuracy.

One of the issues with CCSD(T) is that it is nonvariational due to the inclusion of triple excitations estimated using

perturbation theory. When applied to bond-breaking processes, this results in non-negligible departures from the FCI limit. T1 and D1 diagnostics derived from coupled-cluster amplitudes can be utilized to determine the multireference nature of the system under investigation and the significance of the missing strong correlation. The well-known criteria T10.02 and D10.05, on the other hand, are only valid for organic compounds and should be utilized with caution when applied to transition metal complexes. Alternative diagnostics based on more basic but less expensive concepts produce outcomes that are comparable to the more theoretically sound T1/D1 diagnostics.

Another issue of conventional CCSD(T) is its dependence on basis set size, which consequently leads to large memory and disk space requirements. This bottleneck has been successfully surpassed by explicitly correlated methods, exploration of local nature of correlation, or a combination of both. A few applications of those methods on first-row transition metals have been reported, but their use should be considered carefully when dealing with systems with strong multiconfigurational character. The completely renormalized coupled-cluster scheme of Piecuch and co-workers introduces a strong correlation inside the coupled-cluster framework and has been applied successfully on applications involving transition metals. High-performance computing and linear-scaling methods offer alternative methods for speeding-up quantum chemical calculations for large molecules. Coupling of those methodologies with strongly correlated methods will allow carrying out highly accurate theoretical studies on molecular catalysts.