Commentary

Thermal Corrections in Quantum Chemical Methods and Zero-Point Vibrational Energy

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DESCRIPTION

The analysis of lengthy reaction paths often encountered in catalytic processes demands a faster and implicit technique to rectify the electronic energies for finite temperature effects and calculation of entropic contributions. The 0K energies must first be corrected for the Zero-Point Vibrational Energy before being compared to experimental data (ZPVE). The harmonic approximation is used to compute vibrational normal modes, which is a viable approximation at the equilibrium distances of intermediates and transition states. Furthermore, statistical mechanics can be used to directly compute the finite temperature and entropic adjustments. The molecular partition function may be calculated using these thermal corrections, as well as enthalpies (H) and standard free energies (G). The determination of the first (gradient) and second (Hessian) derivatives of the energy is required for the computation of force constants and, as a result, vibrational frequencies. When applied to structures computed at the same level of theory as the geometric optimization, this phase comprises the transformation of nuclear coordinates to mass-weighted coordinates, which is valid on strongly converged geometries. Because an imaginary frequency indicates that the converged geometry is a saddle-point of the whole potential energy surface, calculating force constants should be utilized as an extra validation of optimized geometries. Despite the fact that most quantum chemistry packages routinely compute such thermochemical corrections following normal-mode analysis, they are only formally valid for gas-phase systems. Even in relatively dilute solutions, their direct use is to predict reaction and activation free energy for processes, only the concentrated multicomponent reactive systems usually seen in real catalysis, which should be done with caution.

Implicit solvation

Because the effect of the solvent molecules can directly or indirectly affect the evolution of a catalytic reaction, it should be incorporated in the modelling of the reaction for homogeneous or heterogeneous catalysts working in liquid phase or in solution. As a result, interactions between solvent molecules and catalyst, reactants, and intermediates should be taken into account for accurate catalyst modelling and quantitative computation of reaction intermediates and reaction barriers.

There are two ways that can be used to relate the quantum-chemical description of the catalyst with the solvent environment. The first is explicit solvation, which takes into account an expanded atomistic model of the catalyst as well as its solvent molecule surroundings. To produce a representative solvation shell or to ensure the availability of specific secondary chemical interactions that could potentially facilitate the examined reaction channels, one expressly adds a sufficient number of solvent molecules around the active site of the catalyst. The catalytic complex and solvation shell are then addressed at the same theoretical level or employing embedding techniques, with the higher level applied to the reactive site and the lower level applied to the solvent molecules. Explicit solvation of the reactive ensemble improves model accuracy at the cost of increased model size and complexity of the reaction channels to be investigated. The implicit solvation models use a continuum mean-field potential to mimic solvent effects, which takes into account the interactions between the solvent and the solvated system. By substituting the solvent molecules with the solution of a classical electrostatic issue, this implicit solvation decreases the computing cost not just by lowering the size of the model, but also, more critically, by reducing the degrees of freedom of the problem (Poisson problem The Conductor-like Screening Model (COSMO), the Polarizable Continuum Model (PCM), and the Parameter-Dependent PCM-type Solvation Models (SMx) have become standard tools for quantum chemists and have been effectively employed in various computational investigations on catalysis. Free energies in ordinary diluted solution can be computed using conventional computational approaches based on these models.

The concept of free energy surfaces could be used to extend the computational study to complex reaction routes in the liquid phase under more realistic conditions (FES). Truhlar and co-workers recently highlighted the relevance of FES in condensed-phase chemistry as an analogue of the potential energy surface used to explain processes in the gas phase. The presence and

type of stationary points on FES in dilute solutions are not directly related to solution concentrations. The major reactivity characteristics, intermediates, and transition states, on the other hand, are directly proportional to concentrations. The free energy correction to account for the realistic composition of the reaction media can range from several kcal mol^{-1} to several kcal mol^{-1}, which is comparable to the characteristic energy barriers for elementary steps in related catalyst systems. Through the analysis of DFT-computed free energy profiles for competing catalytic and deactivation reaction channels, a conceptually similar approach, largely inspired by ab initio thermodynamics methods which are widely used to predict active site composition and evolution in heterogeneous catalysis, and has been used to optimize the performance of a Ru-CNC pincer catalyst in CO_2 hydrogenation. The COSMO-RS method was recently developed to analyze realistic solvents by merging the notion of concentration-dependent free energy surfaces with the realistic description of the solvents. The role of base promoters in ester hydrogenation by Mn-P, N complexes has been successfully revealed using this method.