Alternative Quantum Chemistry Methods for Complex Systems

Dominik Domin[1] , Julien Toulouse[2] and Benoît Braïda[2]
[1]Institut de Chimie Physique, Centre National de la Recherche Scientifique, Université Paris-Saclay, Orsay, France
[2]Laboratoire de Chimie Théorique, Sorbonne Université, Centre National de la Recherche Scientifique, Paris, France

E-mail : dominik.domin@universite-paris-saclay.fr

Studying complex molecular systems, whether in the gas or a condensed phase, requires highly accurate quantum chemistry methods whose computational effort remains tractable when treating realistic systems. Commonly used *ab initio* methods such as Coupled Cluster (CC) or Density Functional Theory (DFT) generally provide reliable results when the underlying approximations and parameterizations are appropriate for the systems being studied. Among the less popular quantum chemistry methods, Valence Bond (VB) theory and Quantum Monte Carlo (QMC) methods, each provides different unique advantages and disadvantages. *Ab initio* VB, while usually only qualitative for energetic properties such as enthalpies of formation, has the distinct advantage of providing very compact wave functions that can be readily mapped into the intuitive Lewis structures that chemists very often use when qualitatively describing the valence electronic structure of atoms and molecules. QMC using trial wave functions based on multireference *ab initio* quantum methods can give some of the most accurate energies and related properties, however, this is often at a great computational cost. Furthermore, the large wave function expansions in the trial function are often difficult to qualitatively interpret. In this lecture, we will present the Valence-Bond Quantum Monte Carlo methods (VB-QMC) which retain the interpretability of VB and the high accuracy of QMC. We will show a few applications which demonstrate their accuracy for molecules in the gas phase and we will examine areas where innovations could be made.