Hybrid quantum/classical and fragmentation techniques for radicals and electronic excited states

Lyudmila V. Slipchenko

Department of Chemistry, Purdue University

560 Oval Drive, West Lafayette, IN 47907, US

Hybrid quantum mechanics/molecular mechanics (QM/MM) and fragmentation techniques allow rigorous description of extended systems including biological polymers and macromolecules. This work focuses on applicability of QM/MM and fragmentation methods to open-shell and electronically excited systems.

In the first part of the talk, we will focus on our recent developments in the Effective Fragment Potential (EFP) method.[1] The EFP method is a model potential designed for describing non-covalent interactions from first principles and without using fitted parameters. When combined with QM subsystem, EFP overcomes the most significant limitations of QM/MM by replacing empirical MM interactions and QM-MM coupling by parameter-free first-principles based ones, while retaining the computational efficiency of QM/MM. We will discuss QM/EFP schemes for electronic excited and ionized states as well as treatment of dispersion in QM/EFP systems.

In the second part, we will talk about our recent work on extending the energy decomposition analysis within the Fragment Molecular Orbital (FMO) method to open-shell systems.[2] In the FMO formalism, one performs fragment calculations in the electrostatic field of other fragments, mutually self-consistent with each other. Extension of the energy decomposition analysis to open-shell states allows one to quantify inter- and intra-molecular interactions in systems containing radicals or high-spin species. The new technique is applied to a tripeptide trialanine upon hydrogen abstraction (HA) from various sites, to characterize and compare the intra-molecular non-covalent interactions in the radical peptide.

[1] Gordon, M.S., Smith, Q.A., Xu, P., Slipchenko, L.V. *Annu. Rev. Phys. Chem.*, 64:553-78, 2013.

[2] Green, M.C., Fedorov, D.G., Kitaura, K., Francisco, J.S., Slipchenko, L.V. *J. Chem. Phys.,* 138:074111, 2013.