Predicting pressure effect on chemical reactions via a unified quantum/classical DFT theory.

The use of high pressures provides a possibility of catalyzing chemical reactions without using high temperatures or expensive and pollutant catalyzers. This kind of “physical catalysis” is able not only to allow reactions which do not occur at ambient conditions, but also to change the stereochemistry of some reactions, like e.g. for Diels-Alder reactions. Understanding the molecular basis of such phenomenon is important to set the best experimental conditions to guide the reaction in the desired direction.

From a theoretical point, the molecular density functional theory (MDFT) is a method deriving from liquid physics theory developed in last years by Borgis, Belloni and co-workers [1-3] which is able to predict the solvation properties of molecules immersed in a solvent at low computational cost. This method can be coupled with a quantum description of the solute molecules, based on electronic DFT (eDFT).

The main goal of the present internship will be to couple eDFT and MDFT for predicting pressure effects on the energy landscape of chemical reactions. We will focus on the simple “physical” Stockmayer solvent, consisting in Lennard-Jones particles with a permanent dipole. The phase diagram is well known and physical properties (compressibility, dielectric constant etc ...) can be tuned easily as a function of molecular parameters (mostly the size of the solvent molecules and their dipole). As a function of the candidate, a theoretical work to conceptualize what means “pressure” in the MDFT formalism can be done.

The first application will be on Diels-Alder cycloaddtions. We will consider a simple model that we have studied by full-atomistic QM/MM simulations[4]. Further, we can apply this approach to study more complex reactions for which QM/MM calculations are too expensive, using the eDFT methods investigated recently by us.[5]

A PhD studentship founded by CEA on the subject is potentially available from October 2023.

Profile: Computational Physics, Statistical Mechanics. The knowledge of scientific programming is a plus.

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The internship will take place at Maison de la Simulation in Paris-Saclay University.

Références :

1) S. Luukonen, M. Levesque, L. Belloni, and D. Borgis. *J. Chem. Phys.* **152**, 064110 (2020).
2) D. Borgis, S. Luukonen, L. Belloni, and G. Jeanmairet. *J. Phys. Chem. B* **124**, 6885 (2020).
3) D. Borgis, S. Luukonen, L. Belloni, and G. Jeanmairet. *J. Chem. Phys.* **155**, 024117 (2021).
4) D.Loco, R.Spezia, I.Chataigner and J.-P.Piquemal. *Chem. Comm.* **56**, 6632-6635 (2020).
5) D.Loco, I.Chataigner, J.-P.Piquemal and R.Spezia. *ChemPhysChem* **23**, e202200349 (2022).