

Campagne 2023 Contrats Doctoraux Instituts/Initiatives

Proposition de Projet de Recherche Doctoral (PRD)

Appel à projet ISCD-Institut des Sciences du calcul & des Données 2023

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

Context and objectives

The use of high pressures provides a possibility of catalyzing chemical reactions without using high temperatures or expensive and pollutant catalyzers. This “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.¹ 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 of view, pressures effect can be modeled either using a fully atomistic description, either by *ad hoc* modification of implicit solvation models. In the first case, this is computationally very costly since the solute should be treated using electronic structure theories and all the solvent molecules should be considered. Recently, QM/MM simulations were used to study a model Diels-Alder reaction under high pressure.² While this approach is intriguing, it clearly suffers by computational limitations. The other typical approach is to use a continuum solvation model, like the popular Polarizable Continuum Model (PCM).³ In this context, Cammi and co-workers have recently adapted it to include pressure effects⁴ and applied to study vibrational properties⁵ and chemical reactions.⁶ In this approach, the solvent is not explicitly present, so the local solute-solvent interactions are missing and, while advanced electronic structure methods can be used for the solute, the solvent description stays at a relatively low level. We should also note that the PCM with pressure effects is present only in developers version of electronic structure codes and not directly available to the community.

An alternative way to theoretically describe solvation is using the molecular density functional theory (MDFT) which is a method derived from theory of liquids developed in last years by Borgis and co-workers.⁷ In this way it is possible to predict the solvation properties of molecules immersed in a solvent at low computational cost with a description of the solvent which is equivalent to what obtained from atomistic simulations. This method can be coupled with a quantum description of the solute molecules, based on electronic DFT (eDFT).⁸ While MDFT was largely developed in last years to study solvation in water, here we will open it to the study of other solvents, and notably **those that are relevant in organic chemistry under high pressure**, like CH₂Cl₂ or toluene.

Furthermore, an important outcome of the project will be a software development to couple MDFT with electronic structure codes and to provide to the community a library which can be used for different purposes.

Working program and organization

The PhD thesis will be composed by two aspects: (1) modeling pressure effects on chemical reactions using eDFT/MDFT; (2) informatics development of a MDFT library compatible with HPC codes. The synergy between the physical-chemistry advisors (RS and DB) with the competences of the informatics component of the team (PT) will be crucial.

1) The pressure effects on equilibrium properties of chemical reactions in solution will be first introduced using solvent models for which the state equations are well known. Firstly, we will focus on Lennard-Jones or Stockmayer (which is constituted by Lennard-Jones spheres with a permanent dipole) fluids. The phase diagrams are well known and it will be easy to vary physical properties as a function of the molecular properties of the solvent (size and dipole). The use of

pseudo-potentials will be considered to specifically treat the short range repulsion between solute and solvent molecules. We will consider Diels-Alder reactions, starting from model ones and then growing in size. Notably, it was shown recently that DFT is able to correctly treat such reactions employing relatively small basis sets (and thus with a low computational effort).⁹

2) The second aspect will be the informatics development to optimize the coupling between the MDFT code with different electronic structure codes. This will be possible thanks to the expertise at Maison de la Simulation (MdlS) to help in scaling MDFT to massive parallel computers and to hybrid CPU/GPU architectures. Specifically, we aim a coupling with codes like CP2K or BigDFT to use the electronic density representation on cartesian grids which is easily compatible with MDFT grid representation. The choice of CP2K or BigDFT will allow a future use on HPC architectures. A final goal of this part will be **to build a general MDFT library** which could be used on different architectures.

Relevance to ISCD

The present project is based on the interdisciplinary collaboration between three fields: theoretical chemistry (RS), theory of liquids (DB) and high performance computing development (PT). An important outcome of the project will be the development of a MDFT-library which would be ready to be coupled to different electronic structure packages. Presently, PCM is the method typically included in different electronic structure softwares: the present project will allow to use also MDFT as an alternative to PCM to describe solvation. In particular the possibility of explicitly considering thermodynamics conditions (here pressure) of the solvent will be a unique feature. The project will be complementary to the actual project funded by iMAT at SU directed by G.Jeanmairet and E.Giner, providing a focus on a different scientific question (pressure effects) and adding a new and different informatics environment. Collaborations and synergies are already planned. The federative context of ISCD will provide an ideal environment for the project and it will also benefit with the collaboration with the Maison de la Simulation in Saclay and other CEA infrastructures in HPC computing. Notably **it will be possible that CEA will co-fund the PhD scholarship**.

PhD advisors

Riccardo Spezia is the leader of the “Dynamics Simulations: Structure and Reactivity” group at LCT and director of CECAM-FR-MOSER node. He is a recognized expert in theoretical modeling of uni- and bi-molecular reactivity, from gas to solution phase. He is the head of the Supporting Team of the general chemical dynamics software VENUS.

Pascal Tremblin is the head of the laboratory Maison de la Simulation in Saclay (CEA, CNRS, UPSaclay). He is an expert in high performance computing and in the development of massively parallel simulation codes.

Daniel Borgis is CNRS research director at PASTEUR laboratory at ENS-Paris and at Maison de la Simulation in Saclay (CEA, CNRS, UPSaclay). He is a world recognized expert in theory of liquid systems and one of the main developers of molecular DFT method.

Student profile

This project will require a student with a background in physics, physical chemistry and/or molecular simulations. Prior experience with molecular dynamics, liquid theory and software development will be a plus.

References (publications by the PhD advisors highlighted in blue)

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- 9) D. Loco, I. Chataigner, J.-P. Piquemal, R. Spezia, *ChemPhysChem* **2022**, 23, e202200349.