

PhD thesis title: Coupling of quantum chemistry models and high-performance algorithms for the global exploration of the energy landscape of atomic and molecular systems

Supervisors:

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Scientific context and objectives:

Investigating the physical and chemical properties of atomic clusters and molecules isolated or in an environment requires the description of these systems at an atomic level. Indeed, essential information (chemical reactivity, thermodynamics, ionization energies, spectroscopy, ...) can be extracted from theoretical chemistry models. This involves: (i) the computation of the potential energy and (ii) the global exploration of the resulting potential energy landscape, possibly containing numerous local minima connected by many transition pathways.

For the energy computation, theoretical models have been developed at different levels of accuracy/resolution. They range from simple descriptions like those based on molecular mechanics, to *ab initio* schemes, solving the quantum Schrödinger equation for electrons. The former allows for the treatment of very large systems. However, the absence of an explicit quantum description of these highly parameterized models prevents their application to all types of systems, and makes it difficult to model certain processes (chemical reactivity, transition between physi- and chemisorption, ...). On the other hand, *ab initio* approaches provide accurate results but at a computational cost that prevent their use for large systems. An interesting intermediate-accuracy approach is the so-called Density Functional based Tight Binding (DFTB) method [1]. It provides a quantum description of the electronic system at a low computational cost due to the use of parameters derived from *ab initio* calculations.

Numerous methods have been proposed to solve energy landscape exploration problem, the most popular ones being based on variants of Monte Carlo (MC) or molecular dynamics (MD) simulation techniques. Despite significant research efforts over several decades, the problem is still open: there is not a general, reliable, and computationally efficient method to globally explore the energy landscape of large systems with a high level of detail. In recent years, algorithms originally developed for robot motion planning have been adapted and applied as efficient methods to explore the conformational space of molecular systems [2]. In particular, the Transition-based Rapidly-exploring Random Trees (T-RRT) algorithm [3,4] has been shown to efficiently explore energy landscapes. Previous work in this context was based on semi-empirical potentials.

The goal of this thesis is to extend these robotics-inspired methods and to combine them in a synergistic manner with DFTB-based models. The main challenge will be to develop algorithmic strategies to reduce the number of single points energy calculations, which is the bottleneck for the application of these models to large systems. A promising approach is to use a multi-model strategy: a simple inexpensive model can be used to approximately explore the landscape aiming to identify low-energy and transition regions, which can be then locally refined using a more accurate model. We recently used this type of approach to investigate the adsorption of sugar molecules on metal surfaces [5]. However, this type of “decoupled” strategy has limitations, since it assumes that the overall topology of the simplified and the “true” energy landscapes are similar. A more intricate combination of models and algorithms, as we aim to do in the context of this interdisciplinary thesis project, requires to guarantee the correctness of the solutions. We will also investigate the combination of the developed algorithm based on T-RRT with other methods. A promising idea is to exploit the global exploratory power of the method to provide a representative set of low-energy (high-probability) transition pathways between different states of the system, and then to refine these solutions using local optimization methods to accurately identify transition states.

During the second half of the project, the developed computational methods will be applied to several systems of interest in collaboration with colleagues at LCPQ. In particular, we will work on the investigation of molecules of astrochemical interest [6,7], and on the characterization of the physicochemical properties of organic micropollutants [8]. Feedback from these use-cases will be useful to improve the methods and the computational tools.

References:

- [1] F Spiegelman, *et al.* (2020) *Advances in Physics: X*, 5:1710252. HAL: [hal-02512933](#)
- [2] I Al-Blawi, *et al.* (2012) *Comput Sci Rev*, 6:125. HAL: [hal-01982596v1](#)
- [3] J Jaillet, *et al.* (2011) *J Comput Chem*, 32:3464. HAL: [hal-01894030](#)
- [4] D Devaurs, *et al.* (2015) *IEEE Trans Nanobioscience*, 15:545. HAL: [hal-01143833v1](#)
- [5] S Abb, *et al.* (2019) *Angewandte*, 58:8336. HAL: [hal-02146428](#)
- [6] M Rapacioli *et al.* (2018) *Phys Chem Chem Phys*, 20:22427. HAL: [hal-01895787](#)
- [7] E Michoulier, *et al.* (2018) *Phys Chem Chem Phys*, 20:1194. HAL: [hal-01764650](#)
- [8] B Belzunces, *et al.* (2016) *J Comput Chem*, 38:133. DOI: [10.1002/jcc.24530](#)

Expected skills:

Strong background in optimization methods and algorithms. Background in physical chemistry, molecular modeling and/or material sciences. Good programming skills, mainly C++. Teamwork skills are also very important for the achievement of the project.

Applications:

Please send an email containing your CV to Juan Cortés (juan.cortes@laas.fr) and Mathias Rapacioli (mathias.rapacioli@irsamc.ups-tlse.fr), indicating in the subject "PhD candidate quantum exploration".