Institut de science des matériaux
ALLIANCE SORBONNE UNIVERSITÉ

AAP 2022 iMAT - Scientific application form

FAQ : https://materiaux.sorbonne-universite.fr/la-recherche/les-appels-projets/faq-et-conseils-pour-deposer-un-dossier-de-candidature

The project should be written in English as it will be read by members of IMAT's international strategic committee. The file must be uploaded on the application form at the following address : https://inscriptions.sorbonne-universite.fr/lime25/index.php/526311?newtest=Y&lang=fr

It should consist of:

1. **Scientific context of project (max. 1,5 pages)**

   - Aim, Context, Scientific approach, Risks, Bibliography. Figures are welcome.
   - Skills and coherence of team

2. **Research plan with provisional calendar (max. 0,5 page)**

3. **Research CV of PI and co-PI's (max. 1 page)**

   - Link to publication list
   - Research domain and skills
   - Grants and theses in course.

Computing RedOx properties in Solution (CREPS)

Scientific context of project (max. 1,5 pages)

The goal of this project is to merge two cutting-edge theoretical methods currently developed in Sorbonne University to develop a new framework that would allow to compute precisely the electronic structure properties of organic and inorganic molecules in solution. We will focus on redox molecules of interest for electrochemical storage devices, such as quinones and TEMPO based molecules.

Solvation effects can have a tremendous influence on chemical reactions and many molecular properties are affected by the choice of the solvent. These experimental observations are not always easy to rationalize and one would benefit from electronic structure calculations to have a detailed picture of the interplay between solvent and solvated species.

Electronic density functional theory (eDFT) is the most widely used method to compute the electronic properties of a molecule because it often gives quite precise results with a moderate computational resources requirement. However, since there is no systematic way of improving the approximations, the quality of the results can be uncontrolled. This is especially true for open-shell systems such as radicals or exotic excited states. A reliable description of these situations requires the use of robust electronic structure methods such as selected configuration interaction (SCI) which make essentially no assumptions on the structure of the wave function and therefore avoids any bias. Although these state-of-the-art calculations can provide a very accurate description of the solute, they are carried in vacuum and at 0 K because of the rapidly growing computational cost. Therefore, solvation effects that can significantly impact these exotic electronic structures are completely disregarded.

To incorporate solvent effects, the most natural choice is to explicitly include solvent molecules into the simulation. This is extremely costly since it increases considerably the number of electrons with respect to in vacuo calculations. The finite temperature is also problematic since the meaningful quantity is no longer the ground state energy but the free energy. This means that the calculation should take place in a statistical ensemble and that a long enough trajectory should be produced to compute ensemble average with good statistics. This is the typical setup of ab initio molecular dynamics (AIMD) calculations. For those two reasons, AIMD simulations are essentially limited to eDFT, and only small systems can be investigated.

The project holder recently proposed an alternative approach to deal with solvent effect in QM calculation based on molecular density functional theory (mDFT) [1]. In mDFT, the solvent molecules are rigid and interact through a classical force field. The solvation free energy and the (3D) solvent structure can be computed by a numerically efficient functional minimization. In this original work, the standard QM/MM partition of the system is used: the QM solute is dealt with eDFT while the surrounding classical water

is treated at the mDFT level.

The objective of this project is use the same approach but using SCI instead of eDFT to describe the QM part of the system. This will allow to tackle open-shell systems and to study their redox properties in solution. Emanuel Giner from the LCT lab will bring his expertise in the development and utilization of SCI [2].

The objective of the project is to compute the redox properties of realistic systems such as the TEMPO and anthraquinone based biredox ionic liquids recently described by Mourad et al [3].
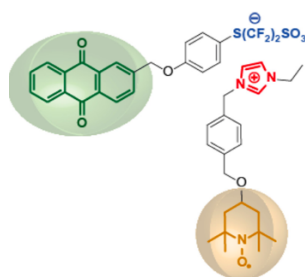

Figure 1: Example of a biredox ionic liquid. The reducible anthraquinone moiety is in green and the oxidizable TEMPO moiety is in orange. Adapted from ref [3].

Research plan with provisional calendar (max. 0,5 page)

From a practical point of view, it is planned to interface the Quantum Package [4], an open-source program with an efficient implementation of SCI with the MDFT program that is able to run mDFT calculation.

First, the PhD candidate will have to get familiar with the two computational program (MDFT and Quantum Package) that are going to be coupled. This step is expected to take 3-6 months. Once this step is completed, he will have to identify the optimal way of doing the coupling, implement it and validate this work on model systems. For this development and validation step, molecular systems similar to the ones used in the original paper [1] will be used. This will allow to choose the optimal grid resolutions, the choice of the functional to describe the solvent and the number of determinant to consider into the SCI wavefunction. This second step is expected to take 12-18 months.

Once confident with our methodology, realistic systems such as the TEMPO and anthraquinone displayed in figure 1 will be addressed. In particular, we will compute the redox potentials and the reorganization free energy of these molecules and compare the theoretical results with experimental data when available. This final step is expected to take 12- 18 months.

[1] G. Jeanmairet, M. Levesque and D. Borgis, J. Chem. Theory Comput. (2020) **16**, 11, 7123–7134
[2] E. Giner, D. P. Tew, Y. Garniron, A. Alavi, J. Chem. Theory Comput. (2018) **14**, 12, 6240-6252
[3] E. Mourad, L. Coustan, P. Lannelongue, D. Zigah, A. Mehdi, A. Vioux, S. Freunberger, F. Favier

and O. Fontaine, Nature Mat. (2017) **16**, 446-453

[4] Y.Garniron *et al.*, J. Chem. Theory Comput. 2019, 15, 6, 3591-3609

Research CV of PI and co-PI's (max. 1 page)

<u>PI</u>: Guillaume Jeanmairet is chargé de recherche in PHENIX (UMR 8234). He is a specialist of molecular density functional theory which he has been developing for almost 10 years.

Publications: https://scholar.google.com/citations?user=HOyQ62QAAAAJ&hl=en

<u>Grants and theses in course</u>: Co-directing PhD of Tzu Yao Hsu. Defense in 2022

He will pass his HDR during this project.

<u>Co-Pi:</u> Emmanuel Giner is chargé de recherche in LCT (UMR 7616). He is an expert of selected CI method and one of the main developer of the quantum package.

Publications: https://scholar.google.com/citations?user=jzaYeosAAAAJ&hl=fr

<u>Grants and theses in course</u>: Co-directing PhD thesis of Diata Traoré. Defense in 2023. He will pass his HDR during this project.

<u>Co-Pi:</u> Mathieu Salanne is Professor in PHENIX (UMR 8234). He is an expert of molecular dynamics simulation of electrochemical devices.

Publications: https://scholar.google.com/citations?user=ZnqXB7kAAAAJ&hl=en

<u>Grants and theses in course</u>:

- Roxanne Berthin (defense in 2022, 50%)
- Camille Bacon (defense in 2022, 50 %)
- Tzu-Yao Hsu (defense in 2022, 100%)
- Xiliang Lian (defense in 2024, 50%)