

PhD thesis: Computing RedOx properties in Solution

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Context and Project

The goal of this thesis 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.

We 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 thesis 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. This will be done in close collaboration with Emanuel Giner from the LCT lab who is an expert in the development and utilization of SCI [2].

The objective of the thesis 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].

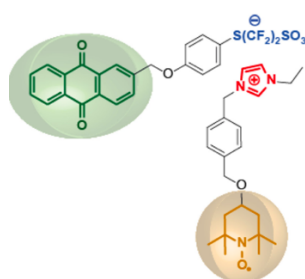


Figure 1: Example of a biredox ionic liquid. The reducible anthraquinone moiety is in green and the oxidizable TEMPO moiety is in orange. Adapted from ref [3].

- [1] G. Jeanmairret, 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

Application

We search for a candidate with skills in theoretical chemistry, physical chemistry and/or quantum chemistry. A experience in coding (Fortran and bash and/or Python) would be appreciated. Interested candidates must contact Guillaume Jeanmairret (guillaume.jeanmairret@sorbone-universite.fr) and Emmanuel Giner (eginer@lct.jussieu.fr) by email, sending a detailed curriculum vitae. We will organize an interview for the pre-selected candidates. The deadline for application is 25/04/2022.