

Simulation of electron transfer reactions using molecular density functional theory

Electron transfer (ET) reactions are involved in a wide range of chemical processes of biological and economical interest. For instance, they are key reactions of the energy conversion process in cells and electrochemical batteries store energy through electron transfer between electrode and electrolyte. Marcus Theory is the widely accepted theoretical framework to describe ET reaction in solution. It has been validated experimentally several times. However, some numerical simulations revealed the existence of ET systems which exhibit a deviation to Marcus Theory. It is in particular true when the redox species is highly confined, for example in a highly disordered porous carbon material. This last example is of particular interest since such materials are widely used as electrodes in electrochemical batteries and capacitors.

Thus, it is essential to be able to study ET reactions without prior assumption about the validity of Marcus Theory. The most widely used approach is to carry simulations using Molecular Dynamics (MD) on half a dozen intermediate states between the oxidized and reduced species. The drawback of this framework is its important computational cost. In the past, several simulations of this type have been realized in the PHENIX lab. Molecular density functional theory (MDFT) is a promising alternative since it allows to obtain results with a precision similar to MD while being faster by several orders of magnitude. In a recent paper (Jeanmairat *et al.*, *Chemical Science*, 10, 2130, 2019), we have shown on model systems that MDFT is relevant to study ET reactions in water.

Our objective is to simulate complex systems: 1) electrochemical devices in order to better understand the role of confinement *i.e.* of the choice of electrodes on the ET reactions and thus on the quantity of energy that can be stored; 2) biological systems to elucidate the role of several ET centres in the energy landscape of electron transport complexes. Note that for the first type of system we need to properly describe the imposed potential difference between the two electrodes, which is already a challenge.

Unfortunately, such systems remain hard to tackle by MD because their size make simulations extremely costly. The MDFT approach would be an excellent alternative but the present algorithm is RAM bounded which prevent the simulation of nanometric systems. The goal of this PhD is to make the study of complex systems by MDFT possible and will require two major numerical development.

1. A first step is to be able to simulate electrochemical devices, where a potential difference is applied between 2 electrodes. Our team is developing the METALWALLS software, an HPC MD code that is able to carry out such simulations. We will first do a sequential coupling of METALWALLS with the MDFT software which will make it possible to run fixed potential MDFT simulations in the short term. The obtained preliminary results will serve as benchmark for the implementation of the fixed potential method within the MDFT framework, to impose the potential self-consistently with the functional optimization. This "all-functional" approach will allow the study the influence of the imposed potential on the kinetic of the ET reaction.
2. To be able to simulate nanometric systems it is mandatory to bypass the current RAM bottleneck of the MDFT software. To do so, we will implement a shared memory algorithm thanks to a hybrid MPI/OpenMP parallelisation of the program to be able to run simulation on HPC architectures.

Once this work will be done, it will become possible to study ET reactions in systems that are currently out of reach. In particular, we will be able to simulate ET reactions in the vicinity of several model of porous carbon electrodes to elucidate the influence of several pore types on the kinetics of ET reactions. We hope that this MDFT approach will become a standard toolbox to gain insight on a wide range of ET processes.

The PhD candidate will run Molecular Dynamics and Molecular Density Functional Theory simulations. Any candidate with a Master in Physical Chemistry, Physics or computer science is encouraged to apply for the position. A previous experience in molecular simulations will be appreciated.

Candidates should send a CV before the 3rd of May 2019 to guillaume.jeanmairat@sorbonne-universite.fr and mathieu.salanne@sorbonne-universite.fr. The PhD will start on October 2019.