Electrochemical nanojunctions: how do they work?

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**2nd supervisor:** Andrew Horsfield (Materials, Imperial College London)

**Collaborator:** Ismael Diez-Perez (Chemistry, Kings College London)

**Abstract**

Electrochemical (EC) nanojunctions (NJ) are promising three terminal functional devices, whose conductance can be modulated through the application of an EC voltage gate. The atomistic understanding of the EC transformation occurring in ECNJ is an almost unexplored niche in computational research and will be the focus of this project.

The non-equilibrium phenomena occurring in ECNJ take place in solution and are driven by the application of an electrochemical potential; double layer effects can create electron screening and additional tunnelling channels, all factors that can affect or even define the electron transmission in the ECNJ. In this project these effects will be modelled explicitly and from a perspective to some extent opposite to that are in molecular electronics, addressing first how the EC environment alters the junction and then electron transport.

To simulate the complex phenomena within ECNJ we will need to perform molecular dynamics under bias and an explicit open-boundary description of the electrons, which must be free to enter and leave the computational cell from source, drain and gate. To this end, the *hair probes* approach[1,2], an open-boundary formalism appropriate for multi terminal electrochemical problems, will be interfaced with DFT and used. To enable the new understanding to be applied to more complex systems, a phase field model will be developed.


**What is the multi-scale nature of the project?**

At the atomic scale we shall use some combination of density functional theory and tight binding. Building on earlier work by one of the supervisors, a phase field type model (with similarities to Poisson-Boltzmann type models) will be developed that can be extended beyond the nanoscale. Parameters within this longer length scale model will be derived from results obtained at the atomic scale.

**How do the expertises of the supervisors complement each other?**
Clotilde S. Cucinotta is an expert in DFT based modelling of charge and mass transfer at the nanoscale, molecular dynamics and molecular electronics.
Andrew P. Horsfield is an expert in TB based methodologies and dynamics of electrons out of equilibrium, and the thermodynamics of complex interfaces.
The experimental collaborator, Ismael Diez-Perez, is an expert in nanoscale molecular EC systems and STM techniques. He will develop prototypic small EC molecular junctions made with synthetic backbones which will allow systematically studying how the EC environment alters the molecular junction and contacts depending upon the chemical nature of the molecular backbone.

**Literature Review**

**Title:** Electrochemical Junctions


**Role of the solvent in determining conductance in small EC junctions dominated by coherent ET:**
- Lambert C., Nichols, RJ. et al., “Gating of single molecule junction conductance by charge transfer complex formation”, Nanoscale, 2015, 7, 18949

**Comparison between tunnelling current between a substrate and a redox molecule adsorbed on its surface with that through a redox molecular junction immersed in an electrolyte**

**Au wires in an EC environment**
- Bing-Wei Mao, Zhao-Bin Chen et al. “Gold atomic contact: Electron conduction in the presence of interfacial charge transfer”, EChem Comm. 2014, 47, 41-44

**MSc Project**
The MSc project will be used as an opportunity to become familiar with the system being investigated and the techniques to be used. To maximise the speed of the simulations we will use tight binding and graphene for the electrodes and the gate.

1. Learn how to use TB code on a graphene system (2 weeks).
2. Generate the structure for a junction with electrodes made of graphene and a carbon nanotube in the gap, equilibrate and compute the current / voltage characteristic of the system (4 weeks).
3. Introduce water for the electrochemical environment, and investigate its influence on the charge transport through the carbon nanotube (6 weeks).
4. Carry out a final analysis of all the data and write the final report (4 weeks).