Nantes Université

Proposition de Stage Master CMT

Stage de M1 ☒ et/ou Stage de M2 ☒

Titre du stage : Photoinduced electron transfer in biomimetic helices

Equipe d'accueil : Modes/CEISAM

Responsable du stage :

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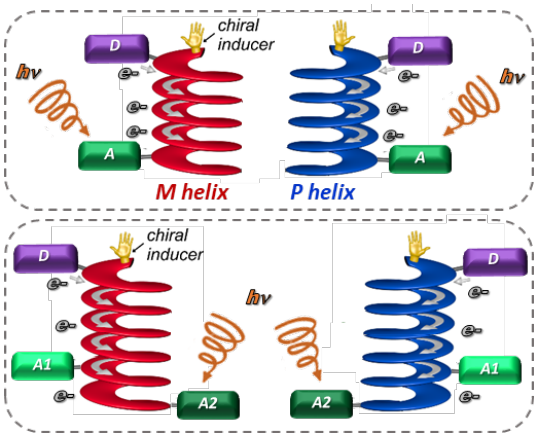
Description du stage proposé :

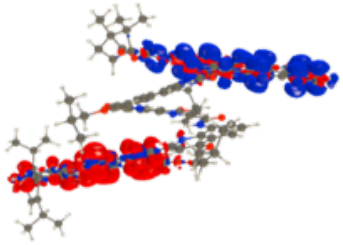
General framework

Photoinduced electron transfer (PeT) is central to many key biological phenomena, such as photosynthesis, enzymatic catalysis of DNA repair, and the working mechanisms of cryptochromes, *i.e.* photosensitive proteins involved in circadian rhythms. The highly efficient biological systems involved in these processes share a common feature: they are *intrinsically chiral* due to their primary sequences (*L*-amino acids) and the associated folded structures. **However, although chirality is recognized as a key factor in many fields of chemistry and biology, its role in PeT processes remains to be fully elucidated**. This internship is proposed in the framework of a large project aiming at shedding light in chirality effects on PeT.



Workplan

During this internship, the student will first benchmark Time-Dependent Density Functional Theory (TD-DFT) using ca. 8 rather compact oligomers (*i.e.,* hexamers and octamers, the smallest of WP1) with various chromophores (location and nature). As reference values, he/she will use either steady-state spectra from experimental partners or theoretical estimates obtained at higher levels of theory. For the experimental data, he/she will compare to measured electronic optical/chiroptical spectra (absorption, emission, ECD) which allows straightforward comparisons between theory and experiment, with vibronic simulations performed in an effective way. Once a proper method is determined the intern will be to establish a relationship between the architecture of the synthesized entities and the possibility to observe PeT. Although, the relative energies and



topologies (spatial positions) of the frontier MOs have been traditionally used to establish the possibility of PeT, such an approach is often insufficient. These calculations will be performed with constrained DFT (C-DFT).

Methods

In practice, the intern will resort to *ab initio* methods having a favorable scaling with system size for performing the calculations. In that context, he/she will mainly use: *a)* density functional theory for ground-state calculations; *b*) time-dependent DFT for modelling optical spectra; *c)* constrained-DFT for investigating PeT as a complementary tool to TD-DFT; and *d*) the polarizable continuum model (PCM) for accounting for environmental effects.

Key objectives

The key objectives will be to

1. determining a computationally-light approach providing trustworthy (semi-quantitative) results.
2. computing PeT rates and establishing structure-property relationships for PeT in long systems.

Expertise

The group has an extensive expertise in the techniques to be applied and used them often, including various TD-DFT schemes and constrained DFT ones.

Methods

During the internship, the student will use *ab initio* methods based on density functional theory (DFT) and wavefunction theories, implemented in programs available in the team. Prior expertise in the field is not necessary; this internship being oriented towards modeling aspects (use not developments).

Collaborations

The group collaborates with Drs. C. Olivier (Bordeaux) on this topic. The internship is supported by the ChiraPeT ANR, led by Dr. C. Olivier.

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