Modelling of Photochemical Reactions through Non-adiabatic Dynamics Simulations

<u>MERRITT Isabella</u>;[A,B] **JACQUEMIN Denis**;[A] **VACHER Nantes**[A]

A) Laboratoire CEISAM, Université de Nantes, 2 Rue de la Houssinière; 44300, France ;
B) Institut de Sciences Moléculaires, Université de Bordeaux, 351 Cours de la Libération, 33405, France.

isabella.merritt@u-bordeaux.fr

Photochemical reactions, triggered after absorption of a photon, hold great potential for a wide range of applications, opening up otherwise impossible reactive pathways, expanding chemical space, and offering routes for green synthesis. The control of molecular structure using light in light-controlled molecular switches, known as photochromes, can be used for novel applications, such as smart materials, or light-controlled drug delivery.[1] Understanding the mechanisms underlying photochemical reactions can enable the intelligent selection and design of molecules for such applications. Studying these reactions theoretically requires a specialized toolbox of methods, especially since the majority of photochemical reactions are what we call "non-adiabatic", meaning they involve radiationless transitions between electronic states. The most powerful methods in the theoretical toolbox to deal with such reactions are non-adiabatic dynamics (NAD). These methods allow for a time-dependent modelling of the mechanisms underlying photochemical reactions, while accounting for the breakdown of the Born-Oppenheimer approximation which leads to non-adiabatic processes.

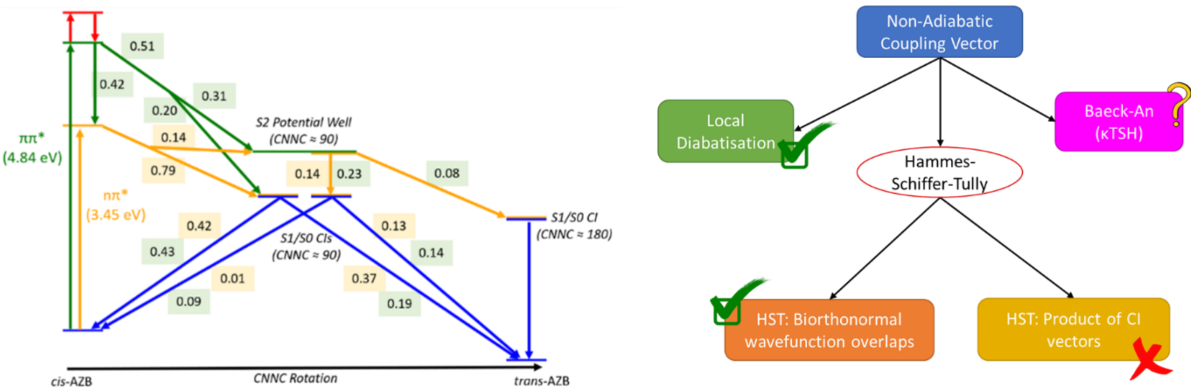

Figure 1. *Left*: Relaxation pathways of *cis*-azobenzene ; *Right:* Different approximate approaches to TSH.

In this presentation, I will first demonstrate the potential of NAD methods as powerful tools to complement experiment and to understand and predict properties and mechanisms of photochemical reactions. To this end, I will discuss primarily the modelling of the azobenzene photochrome, where theoretical modelling[2] using NAD allows for an explanation of the lower quantum yield experimentally measured after excitation to the second (ππ*) compared to the first (nπ*) excited state.[3] After demonstrating the potential of NAD simulations, I will discuss some different approaches to the popular Trajectory Surface Hopping (TSH) method. By presenting the impact approximations can have on the final results for a set of photochemical reactions, I will demonstrate the importance of rigorous testing for such simulations, as well as the potential for cheaper NAD simulations.[4]

<u>Keywords</u>: photochemistry, excited states, non-adiabatic dynamics.

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