

Role of electron-nuclear coupled dynamics on charge migration in glycine induced by attosecond pulses

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Synopsis We theoretically investigate the charge migration process initiated by an attosecond XUV pulse in the glycine molecule. We show that, for the chosen pulse, charge dynamics in glycine is barely affected by nuclear motion or non adiabatic effects during the first 8 fs, and that the initial electronic coherences do not dissipate during the first 15-20 fs. In contrast, small variations in the initial nuclear positions, compatible with the geometries expected in the Franck-Condon region, lead to noticeable changes in this dynamics.

Quantum Mechanics states that the expectation value of an hermitian, time independent operator will exhibit a temporal dependence if the system is described by a non-stationary state of that operator. In other words, any superposition of eigenstates of a given system leads to a time-varying observable, such as the probability density. This lies at the core of the so-called ultrafast charge migration, concept introduced by Cederbaum and Zobeley in the nineties to describe the charge fluctuations occurring in the attosecond time scale upon sudden ionization of a molecule [1]. Investigations of ultrafast charge migration were partly inspired by the pioneering work of Weinkauff and coworkers on peptides chains [2]. However, the first experimental observation of this phenomenon obtained with attosecond resolution has only been achieved in 2014 for the amino acid phenylalanine [3]. New theoretical approaches are being developed to provide a solid knowledge of these ultrafast light-induced processes.

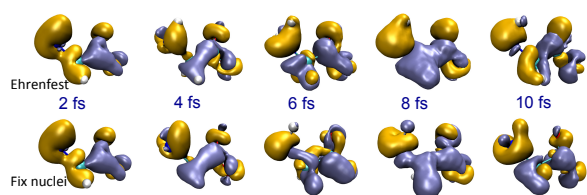


Figure 1. Spin density changes as a function of time after the interaction of the ultrashort pulse for the TDDFT simulations using the Ehrenfest approach (upper row) and frozen nuclei (lower row).

Most of existing methods describe the process by assuming ionization as a sudden transition from the ground state, avoiding the evaluation of ionization amplitudes [4, 5]. And, even in those works where

the ionization step is more accurately represented [3, 6], the nuclei remain frozen, which is expected to be a reasonable approximation in the first tens of femtoseconds [7, 8]. In this conference, we will present our progresses to achieve a complete theoretical description of the ultrafast charge migration triggered in glycine molecule, which include both an accurate evaluation of the ionization step and the nuclear degrees of freedom in the time propagation. We employ a Static-exchange DFT-based approach [9] to extract reliable ionization amplitudes, while the correlated electron-nuclear dynamics of the ionic subsystem is obtained from a TDDFT-Ehrenfest simulation. The resulting time evolution of the electronic density is shown in the upper row of Fig. 1 and compared with the result of a fixed nuclei approach (upper row). Frozen nuclei approaches are thus validated within the first 10 fs. We will also show recent simulations to demonstrate how the choice of the ionizing laser pulse modifies the ensuing charge dynamics, thus opening the door to the control of charge-directed reactivity in biologically relevant molecules.

References

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