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# Theoretical Study of Ultrafast Electron Dynamics in Amino Acids

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**Synopsis** Prompt ionization of large biological molecules may induce ultrafast charge migration along the molecular skeleton, preceding any nuclear rearrangement[1, 2]. This phenomenon has been recently observed in the amino acid phenylalanine [3] in a two-color pump probe experiment, where the production of ionic fragments was measured as a function of the time delay between the two pulses and charge fluctuations manifested as sub-4.5 fs oscillations in the quantum yield of a specific doubly charged fragment. We present our latest results in glycine, and compare with previous findings in phenylalanine [3]. We seek to perform a systematic study including larger aminoacids such as tryptophan.

The development of attosecond technology has enabled the real-time observation of electron motion in atoms, molecules and condensed matter [4]. In the case of large biological systems, such as amino acids, sudden ionization from a molecular orbital may trigger an ultrafast electronic response which is solely driven by electron correlation, as predicted in various theoretical works [1, 2]. However, due to the large bandwidth of attosecond pulses employed in state-of-the-art experiments [3, 4], electrons are usually removed not from one but from many orbitals, thus leading to a coherent superposition of ionic states. Therefore, an accurate description of the ionization process becomes crucial in the description of these experimental observations.

We have performed a theoretical study of the field-free evolution of the electronic wave packet generated in amino acids (glycine, phenylalanine and tryptophan) upon the interaction with with attosecond pulses. The ionization amplitudes have been quantitatively determined for all open channels using the static-exchange DFT method [5] developed by Decleva and collaborators, which makes use of the Kohn-Sham DFT to describe molecular bound states and of the Galerkin approach to evaluate continuum wave functions in the field of the corresponding Kohn-Sham density. The evolution of the electronic wave packet has then been described by using a standard time-dependent density matrix formalism. The results of the numerical simulations clearly show the production of an ultrafast electronic response occurring in a sub-femtosecond time scale and are in good agreement with recent experimental observations [3]. We notice that, in contrast with most previous works, most valence and inner-valence electrons are efficiently ionized and therefore the observed dynamics is that of a delocalized hole. We have further analyzed the role of the emitted electron in the hole migration mechanism and observed that even faster charge fluctuations (faster than the experimental resolution) might arise as a consequence of the interplay between the ground and continuum states.

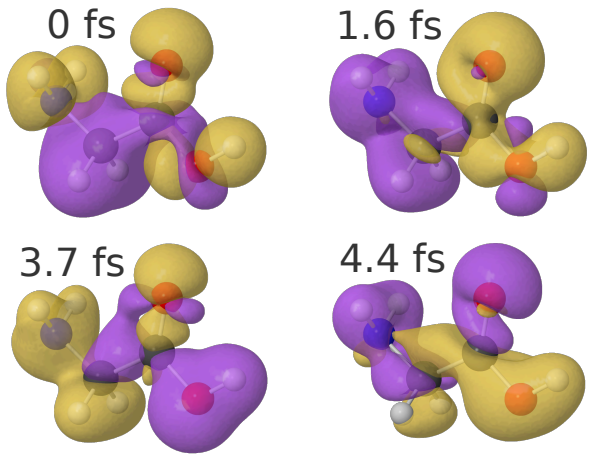


**Figure 1**. Relative variation of the hole density generated by an attosecond XUV pulse in the amino acid glycine with respect to its time-averaged value (yellow: $10^{-4}$a.u., purple: $-10^{-4}$a.u.). Time is refereed to the end of the pulse.

## References

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