

# Coupled electron-nuclear dynamics following valence ionization of toluene

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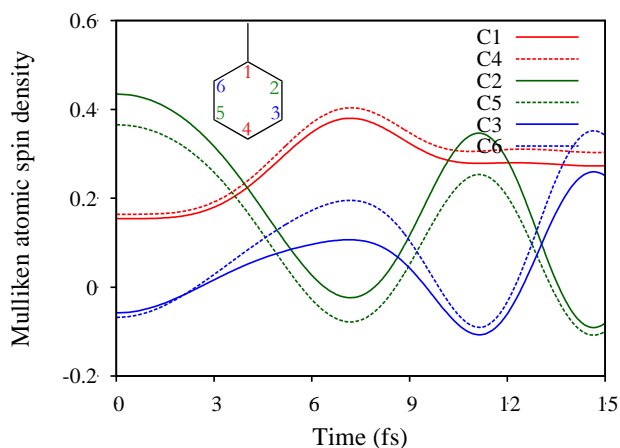
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## Abstract

Photoionization can initiate electron dynamics in molecules. Theoretical studies at a single fixed nuclear geometry have demonstrated oscillatory charge migration. Here, we show how nuclear motion and the initial nuclear distribution affect the outcome of electron dynamics. In toluene, only a few fs are necessary for the nuclear geometry to distort enough to affect both the time scale and nature of electron dynamics following valence ionization. We also show how by choosing the initial weight and phase of a superposition of electronic states, one can control the initial nuclear dynamics.

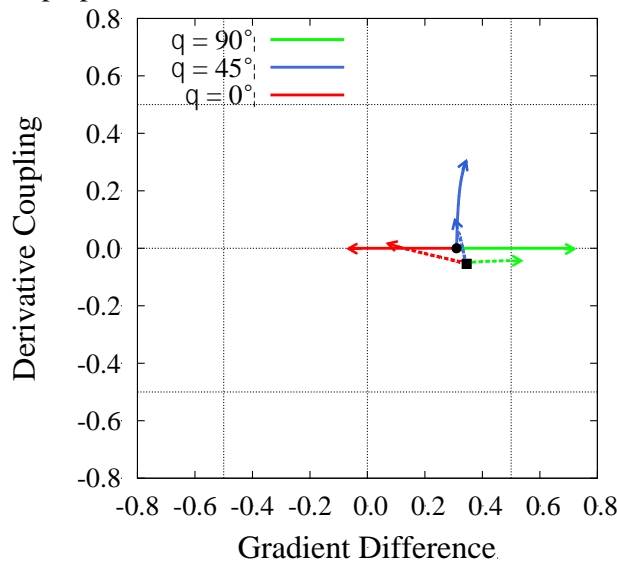
Photoionization can create a coherent superposition of electronic states and therefore initiates electron dynamics in molecules. Observing and controlling this experimentally is a target of attosecond spectroscopy. Theoretical studies at a single fixed nuclear geometry have demonstrated oscillatory charge migration [1]. Using a CASSCF implementation of the Ehrenfest method [2], we can study the evolution of a non-stationary electronic wave function for fixed nuclei, and where the nuclei are allowed to move, to investigate the differences [3-4]. We show the effect of sampling the initial geometry on both electron and coupled electron-nuclear dynamics, with a Wigner distribution to mimic the zero-point energy [5].

The method has been used to investigate dynamics of toluene cation (a substituted benzene) because vertical ionization takes place at a geometry slightly displaced from the conical intersection between ground and first excited states of the cation. In toluene cation, only 2-3 fs are necessary for the nuclear geometry to distort enough to affect both the time scale and nature of electron dynamics (Figure 1) [6]. Sampling changes the initial energy gap between the electronic eigenstates and therefore the time scale of electron dynamics.



**Fig. 1.** Evolution of spin densities after ionization of toluene (nuclear motion included). The initial electronic wave function is  $1/\sqrt{2}(|\psi_0\rangle + |\psi_1\rangle)$ .

We systematically investigated the effect of changing the relative amplitude and phase in the initial superposition of electronic states. By controlling the initial electronic conditions in this way, we can control the subsequent initial nuclear motion. For example, if vertical ionisation of toluene prepares an equal superposition of the two lowest energy states, the nuclear relaxation takes place in a direction orthogonal to the adiabatic dynamics, following the gradient of the superposition [5].



**Fig. 2.** Nuclear trajectories in the branching space (5 fs) initiated with  $|\psi_0\rangle$  in green,  $1/\sqrt{2}(|\psi_0\rangle + |\psi_1\rangle)$  in blue, and  $|\psi_1\rangle$  in red: (dashed lines) average for the ensemble of trajectories and (solid lines) unsampled trajectory.

## References

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