# The Quantum-Ehrenfest Method with the Inclusion of an IR Pulse: Application to Electron Dynamics of the Allene Radical Cation

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Abstract

We describe the implementation of a laser control pulse[1a] in the Quantum-Ehrenfest method[1], a molecular quantum dynamics method that solves the time-dependent Schrödinger equation for both electrons and nuclei. The oscillating electric field-dipole interaction is incorporated directly in the one-electron Hamiltonian of the electronic structure part of the algorithm[1b].

As an illustration a simple model of a pump-control experiment, we shall present the coupled electron-nuclear dynamics of the $\pi$-system in allene radical cation $(\bullet CH_2{=}C{=}CH_2)^+$. We start (pump) with a two-state superposition of two cationic states. The resulting electron dynamics corresponds to rapid oscillation of the unpaired electron between the two terminal methlylenes. This electron dynamics is in turn coupled to the torsional motion of the terminal methylenes. There is a conical intersection at $90^o$ twist where the electron dynamics collapses because the adiabatic states become degenerate. After passing the conical intersection the electron dynamics revives.

The IR pulse (control) in our simulations is timed to have its maximum at the conical intersection. Our simulations show that the effect of the (control) pulse is to change the electron dynamics at the conical intersection and, as a consequence, the concomitant nuclear dynamics which is dominated by change of the torsional angle

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