
Coupled electron-nuclear dynamics following photoionisation of benzenes

Morgane Vacher*¹, David Mendive-Tapia , Jan Meisner , Michael Bearpark , and Michael Robb

¹Department of Chemistry, Imperial College London – Royaume-Uni

Résumé

Photoionisation can create a coherent superposition of electronic states and therefore initiates electronic dynamics in atoms and molecules. Observing and controlling this experimentally is a target of attosecond spectroscopy.

Theoretical studies of pure electron dynamics at a fixed nuclear geometry have demonstrated oscillatory charge migration. Using a CASSCF implementation of the Ehrenfest method, we can study the evolution of a non-stationary electronic wavefunction where the nuclei are allowed to move. The method has been used to investigate dynamics upon ionisation of small organic molecules. We choose benzene as a prototype because ionising the neutral species leads to a Jahn-Teller degeneracy between ground and first excited states of the cation.

In all of our calculations, the initial geometry is the equilibrium geometry of the neutral species. The simulations were initially started with equal populations of ground and first excited states, with no deliberate relative phase between them. With nuclei fixed, there is no electron dynamics in this case. However, if we add substituents that break symmetry but do not radically alter the electronic structure, we see charge migration.

We systematically investigated the effect of changing the relative amplitudes and phases in the initial superposition of electronic states. By controlling the initial electronic conditions, we can control the subsequent initial nuclear motion. For example, relative real phase allows us to predict which minimum on the ground state potential energy surface we decay towards; complex phase can be chosen such that the system remains with the degenerate intersection space for at least 5 fs.

Our calculations have explicitly shown how changing the initial electronic wavefunction can control nuclear dynamics for an ionised molecule where multiple electronic states are close in energy. For benzene cation we have also been able to show how chemical substitution affects the outcome of the electronic dynamics.

Mots-Clés: electron dynamics, nuclear dynamics, Ehrenfest method, charge migration

*Intervenant