Coupled electron-nuclear dynamics using a second-order CASSCF implementation of the Ehrenfest method

David Mendive-Tapia[1], Morgane Vacher[2], Jan Meisner[3], Michael J. Bearpark[2], and Michael A. Robb[2]

[1]*Institut Charles Gerhardt - UMR 5253, Université Montpellier 2, France*
david.mendive-tapia@univ-montp2.fr
[2]*Department of Chemistry, Imperial College London, United Kingdom*
m.bearpark@imperial.ac.uk; mike.robb@imperial.ac.uk
[3]*Institute of Theoretical Chemistry, University of Stuttgart, Germany*

The recent development of attosecond laser technology begins to provide the experimental technology for direct time domain measurements for the electronic motion in molecules.[1] If an electron is "suddenly" removed from a molecule by ionisation it will find itself in a superposition of electronic states, which is predicted to be followed by a migration of electric charge within the molecule. A number of theoretical studies of pure electron dynamics at a fixed nuclear geometry have demonstrated this oscillatory charge migration.[2]
However after sudden ionisation, the gradient with respect to the nuclear motion will not be zero, since the equilibrium geometry of the ionised state and the neutral state would be different. Thus, the geometry of the molecule must change and evolve in time as well.[3] Here we address this by including the effect of nuclear motion via a CASSCF implementation of the Ehrenfest method.[4]
Our recent work in substituted benzene cations shows how:
i) Changes in the energy gap between electronic states affects the time-scale of the electronic dynamics.[5] ii) Changes in the initial electronic wave function can control the "direction" of the subsequent nuclear dynamics.[6]

References

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