On-the-fly *ab initio* semiclassical evaluation of electronic coherences in polyatomic molecules

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Ionization of molecules very often leads to simultaneous population of several cationic states launching thus pure electron dynamics that appear as ultrafast migration of the hole charge throughout the system. A crucial question in the emerging field of attochemistry is whether these pure electronic coherences last long enough to allow for their efficient observation and eventual manipulation with ultrashort laser pulses.
In order to address this question a full quantum treatment of the coupled electron-nuclear dynamics is required. Despite the fact that such calculations were recently performed using MCTDH-based approaches for several small molecules [1-3], it is still very case specific and requires construction of global PES, which is a daunting task by itself.
In contrast, approximate semiclassical methods can be used in combination with on-the-fly evaluation of the electronic structure which allows to avoid the exponential scaling problem. One of the simplest, yet efficient, semiclassical approaches for molecular dynamics is provided by the thawed Gaussian approximation (TGA) developed by Heller and co-workers [4]. Within this approach, the nuclear wavefunction is described by a single Gaussian wave packet whose time-dependent width is propagated using the local harmonic approximation of the PES.
Here we present a semiclassical TGA calculations of the electronic coherences initiated by outer-valence ionization of propiolic acid molecule. A very good agreement between fully quantum MCTDH calculations and semiclassical TGA results is demonstrated. We argue that simple semiclassical schemes can be efficiently used to support theoretically recent experimental studies of ultrafast electronic dynamics in realistic molecular systems.

References

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