

Exploiting electronic entanglement for steering selective quantum dynamics in molecules pumped by ultrashort optical pulses

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Short attosecond (as) or few femtoseconds (fs) pulses have a broad energy bandwidth which allows exciting a superposition of several electronic states in neutral molecules and molecular cations. The nature of the states excited (valence, Rydberg) can be controlled by tuning the pulse parameters. This opens the way to novel avenues for control by engineering of electronic coherences between selected electronic states to steer charge migration through the selective localization the electronic density on its purely electronic time scale.¹ As the nuclei begin to move, the electronic and nuclear motions are entangled and the engineered electronic coherences can be usefully exploited for steering the vibronic density through the network of non adiabatic interactions to specific products.

In order to design control schemes built on a selective photoexcitation of electronic coherences, we analyze the time evolution of the entanglement between nuclear and electronic degrees of freedom using singular valued decomposition (SVD) of the wave function.²

I will discuss several examples of the role of initial entanglement induced by the interaction with an attopulse in the selective fragmentation of diatomic molecules,³ the bond formation in a 4C ring closure induced by tuning the parameters of a few cycle deep UV pulse⁴ and the time evolution of the entanglement in the ultrafast structural rearrangement of the methane cation ionized to a superposition of its three lowest electronic states.⁵

References

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