

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

Content

Photoexcitation or photoionization by short attosecond (as) or few femtoseconds (fs) pulses build a superposition of the electronic states that fall within the broad pulse energy bandwidth. By tuning the pulse parameters, one can engineer electronic coherences between selected electronic states and control the charge migration and the spatio-temporal beating of the electronic density on a 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.[2,3] We discuss three recent dynamical computations for which we analyze the time evolution of the entanglement between nuclear and electronic degrees of freedom using singular valued decomposition (SVD) of the wave function.[4,5] At each time step, the wave function is thereby written as a superposition of singular states weighted by their corresponding singular values ordered by their decreasing magnitude. Each singular state is a product of a component that depends only on the nuclear degrees of freedom and a component depending on the electronic coordinates. This singular state is a separable wave function. When more than one singular state is necessary for describing the wave function, it is entangled. This analysis gives valuable insights on how the entanglement of the initial state governs its subsequent modulation by the nuclear motion on coupled electronic states. It is the initial entanglement that can be controlled by the excitation pulse. We first compare the entangled electron-nuclei dynamics in two diatomic molecules, LiH and N₂, excited by short 2fs UV pulses. In LiH, the targeted electronic states are shallow and dissociative for the energy range span by the broad energy bandwidth of the 5 eV – 2fs pulse and the non adiabatic interactions (NAC) are rather weak. Our results show that a few singular states are necessary for accurately describing the time evolving wave function and that their number is modulated in time by the interplay between the gradients of the potential energy curves of the excited states and the NAC between them driven by the nuclear motion.[4] In N₂,[6] we targeted with the pulse a superposition of the three lowest Σ states, two Rydberg states and a shallower valence state, strongly coupled by NAC at the exit of the Franck-Condon region. In that case, there is a strong modulation in time of the entanglement due to the NAC coupling.[5] If time permits, we will also report preliminary results on 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.[2]

References

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