Velocity adjustment in surface hopping

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Surface hopping simulates nonadiabatic dynamics by evolving a swarm of independent trajectories involving multiple electronic states. Trajectories are propagated on a single surface, and hops between them are based on a stochastic algorithm. This surface change occurs at small but finite potential energy gaps when the potential energy instantaneously changes. Therefore, to ensure total energy conservation during the dynamics, the nuclear kinetic energy must be changed to compensate for the potential energy variation. The proper way to change the kinetic energy is by rescaling the nuclear velocities in the direction of the nonadiabatic coupling vector. However, in many cases, those vectors are not available. Thus, what are the alternatives to rescale velocities? A common choice is the momentum direction, but this can induce an abnormal amount of back hoppings, leading to unphysical dynamics. In this work,[1] we compared different ways of rescaling the velocity after a hooping occurs, taking fulvene and a protonated Schiff base (PSB4) as examples, assessing their population decays and reaction yields. The different sets of dynamics have the velocity adjusted in either nonadiabatic coupling (**h**), gradient difference (**g**), or momentum directions (**p**-fullKE). For the latter, in addition to the conventional algorithm, we explored the performance of a reduced kinetic energy reservoir approach recently proposed[2] (**p**-redKE). Our results show that the dynamics of fulvene (Figure 1) is susceptible to the velocity adjustment chosen, but *cis*-PSB4 is not. We correlate this result to the topographies near the conical intersections. When nonadiabatic coupling vectors are unavailable, the **g** direction is the best adjustment option. If this is also not available, a semiempirical vector direction (**h**-FOMO-CI) or the **p**-redKE direction become an excellent option to prevent an artificial excess of back hoppings. We conclude that the precise velocity adjustment direction is less crucial for describing the nonadiabatic dynamics than the kinetic energy reservoir's size.

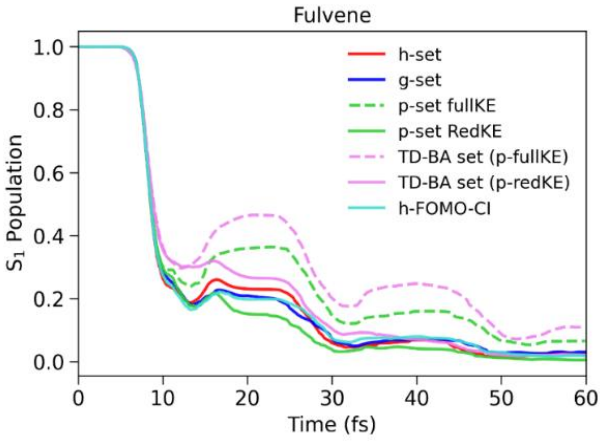

Figure 1. Excited state population evolution of fulvene computed with different velocity adjustments.

Keywords: Excited state dynamics, surface hopping, conical intersections.

[1] J. M. Toldo, R. S. Mattos, M. Pinheiro, S. Mukherjee and M. Barbatti, *J. Chem. Theory Comput.* 20 (2024) 614-624.

[2] G. Braun, I. Borges, A. J. A. Aquino, H. Lischka, F. Plasser, S. A. do Monte, E. Ventura, S. Mukherjee and M. Barbatti, *J. Chem. Phys.* 157 (2022) 154305.