

# Simulating Attochemistry: Which Dynamics Methods to Use?

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Since the advent of the first attosecond pulse in 2001,<sup>1</sup> its application on polyatomic molecules has given birth to the field of attochemistry. The large energy bandwidth of such laser source will coherently populate multiple electronic states i.e. a coherent electronic superposition. A particular challenge of this field is the accurate theoretical simulation of the molecular coupled electron-nuclear dynamics induced by an electronic wavepacket. Using an example system with two cationic electronic states of fluorobenzene where a conical intersection is located in the vicinity of the Franck-Condon point (FC), we assess the accuracy of mixed quantum-classical methods such as Tully surface hopping and classical Ehrenfest for attochemical simulations. For the reference quantum wavepacket dynamics, we use Direct Dynamics variational Multiconfigurational Gaussian (DD-vMCG) method<sup>2</sup>. Upon coherent ionization to the two lowest cationic states, mixed quantum-classical methods with independent trajectories predict inaccurate trends for the nuclear dynamics and heavily underestimate the contribution of the derivative coupling to the average nuclear motion compared to the full quantum dynamics.<sup>3</sup>

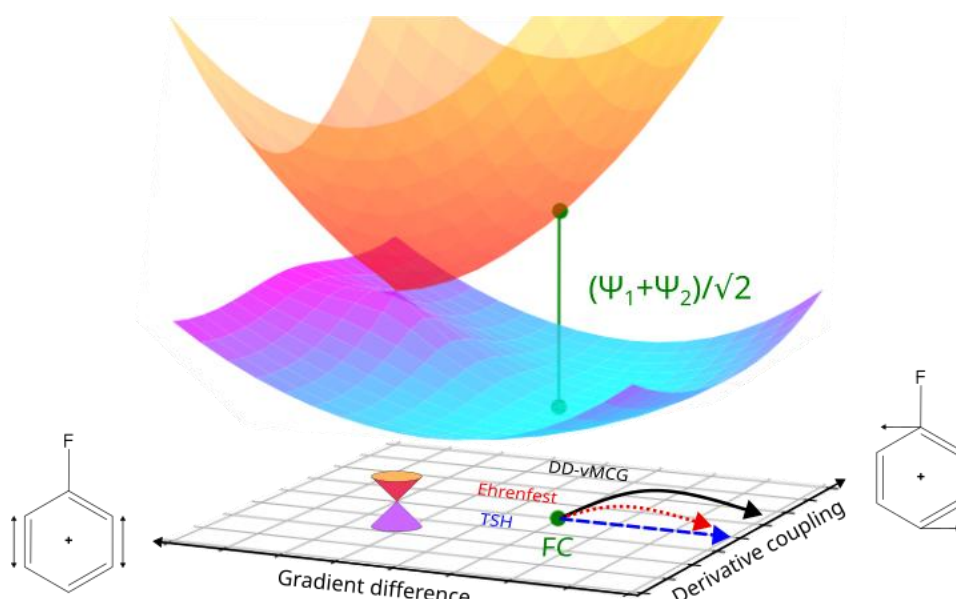


Figure 1. Scheme showing the average nuclear dynamics in the branching space, gradient difference and derivative coupling coordinate, induced by an initial electronic coherent superposition at the neutral Franck-Condon point using the Tully surface hopping, classical Ehrenfest and DD-vMCG methods

**Keywords:** attochemistry, nonadiabatic dynamics, computational chemistry

<sup>1</sup> P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H. G. Muller, P. Agostini, *Science* 292 (2001) 1689–1692.

<sup>2</sup> G. A. Worth, I. Burghardt, *Chemical Physics Letters* 368 (2003) 502-508.

<sup>3</sup> T. Tran, A. Ferté, M. Vacher, *The Journal of Physical Chemistry Letters* 15 (2024) 3646-3652.