Nonadiabatic dynamics with stochastic electronic structure forces

Shervin Fatehi[a]

[a] *The University of Texas Rio Grande Valley*
shervin.fatehi@utrgv.edu

Over the past several years, the present author has been concerned with several questions surrounding the feasibility of large-scale nonadiabatic dynamics calculations with *ab initio* forces. Briefly stated, these questions are: First, can we afford to do the dynamics (*i.e.,* can we reduce the cost of each molecular dynamics step) [1]? Second, are the states involved ordered properly (*i.e.,* as given by an affordable electronic structure theory) [2]? Third, can we afford to compute couplings between the states (*i.e.,* are analytical approaches available and implemented) [3–5]? Fourth, are the couplings physically sensible (*i.e.,* can they be corrected for spurious couplings that may arise from center-of-mass motion) [6]?

Together with co-workers from the Universities of Pennsylvania and Utah, we have provided affirmative answers to all of the above questions. Now I have turned my attention toward extending these successes to the range of stochastic electronic structure techniques that have come into use over the last decade, including full configuration-interaction quantum Monte Carlo methods and stochastic coupled-cluster approaches. In this poster, I will present some developments in this direction and indicate next steps.

In addition to the main scientific content given above, I may present letter-sized mini-posters touching on other research in my group at the University of Texas Rio Grande Valley. Areas of interest include energy transfer following core excitation in the condensed phase, numerical methods for the determination of steric hindrance, and fundamentals & applications of nonadiabatic phenomena in mechanochemistry.

References

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