How Progressive Excited-State Molecular Dynamics Is?

Lessons from the Cyclobutanone Prediction Challenge

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ABSTRACT

The philosopher of science Imre Lakatos proposed that we should judge a research program as progressive if it predicted novel empirical facts and that at least some could be tested. If not, the program is degenerating. Excited-state molecular dynamics constitutes a research program in Lakatos' sense of a core set of theoretical assumptions (the Born-Oppenheimer separability, for example) surrounded by a protective belt of auxiliary hypotheses (the need for nonadiabatic corrections).

In 2023, The Journal of Chemical Physics proposed a double-blind prediction challenge to forecast the outcomes of an upcoming experiment using ultrafast electron diffraction. A gas sample of cyclobutanone would be irradiated with a 200 nm light source targeting the Rydberg excited state ($n \rightarrow 3s$), and electron diffraction images would be collected in variable step sizes. Theoreticians were invited to publish their simulations in a special issue, where only then would the experimental results be revealed.

Fifteen groups, ours inclusive, answered the challenge in early 2024. They submitted excited-state molecular dynamics simulations based on quantum wave packet propagations, multiple spawning, multiple cloning, Ehrenfest, and diverse surface hopping approaches. These simulations employed electronic-state surfaces computed with many quantum-chemical methods ranging from TDDFT to CASPT2. This talk will discuss these results and address Lakatos' demarcation criterion in excited-state molecular dynamics.