Propagation Of Ab-Initio Quantum Dynamics

Simulating the excited state dynamics of molecules, which is important for spectroscopy or photochemistry, requires the propagation of electronic and nuclear wavefunctions from the molecular time-dependent Schrödinger equation. Tully's fewest switches surface hopping (FSSH) algorithm is used for non-adiabatic molecular dynamic (NAMD) simulations because it does not require explicit propagation of nuclear wavefunctions. Instead, it expands the electronic wavefunction in the Born-Oppenheimer (BO) basis to yield a matrix equation that propagates a time-dependent amplitude vector based on the electronic wavefunction, in which a switch or hop from one BO state to another occurs in regions of strong coupling. In time-dependent density function theory (TDDFT), the formal solution to this equation can be described as a unitary propagator acting on an initial wavefunction. However, this propagation is currently limited by the size of the time step due to larger time steps causing larger propagation errors. A combination of Gaussian quadratures and mimetic methods, which focus on building operators that are discrete analogs to continuum mechanics, should lessen propagation errors and display a conservation of energy and wavefunction norms. Thus, the aforementioned methods combined with enforcing the necessary symmetries should allow for higher-accuracy propagations of the electronic wavefunction when using larger time steps.

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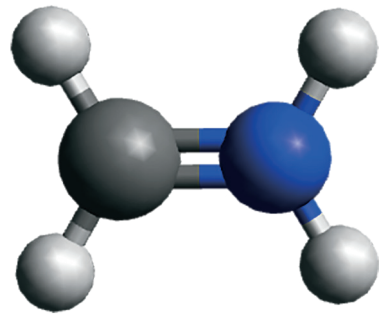
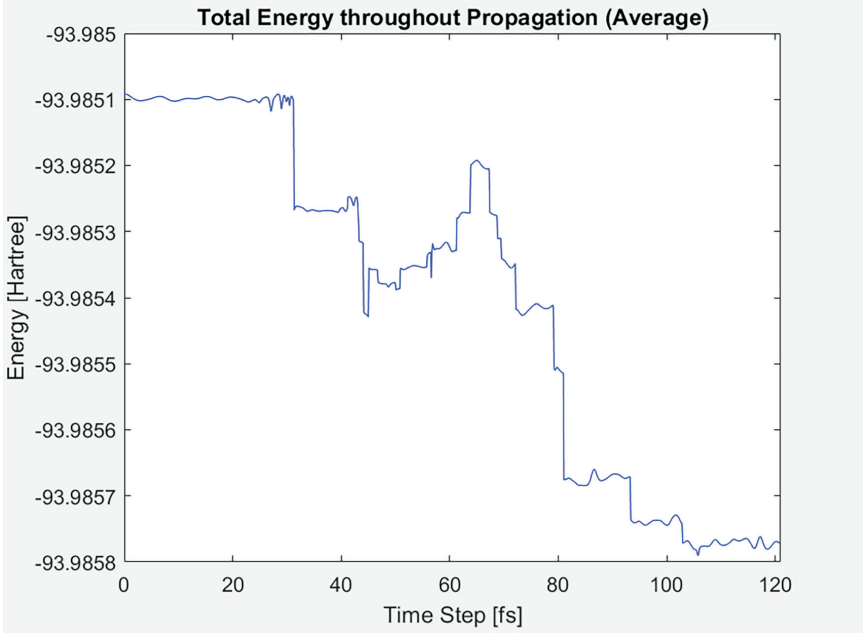
This research is supported by the Department of Chemistry at University of CA, Irvine and the Computational Science Research Center (CSRC) at San Diego State University

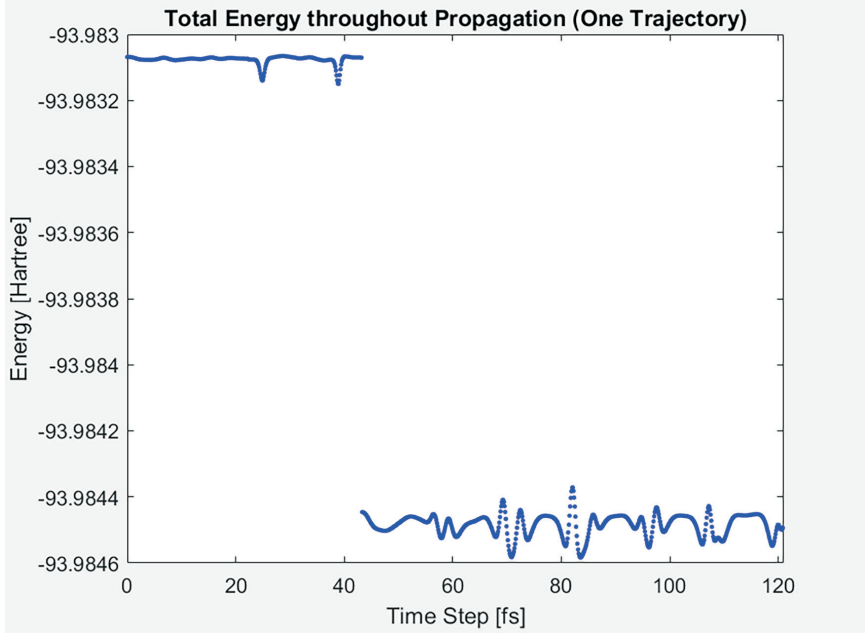
A suite of 30 NAMD simulations (trajectories) with surface hopping are run on TURBOMOLE for a formaldiminium molecule



Initial Conditions:
All trajectories start at the S1 Franck-Condon geometry at t = 0 and are propagated using a time step of 0.121 fs for a total time period of 121 fs. All simulations are run using def2-SVP basis set and C1 symmetry.



Averaging the trajectories in the suite, an overall decrease in energy is observed (~4 kcal/mol loss in energy).



Investigating further, total energy is not conserved and is discontinuous during a surface hop.

Considerations for Another Implementation

- Errors in the propagation could occur from finite differencing errors that accumulate as the time step progresses.
- Due to the discontinuity caused by surface hopping, time-reversal symmetry is not obeyed and should be enforced.
- Based on individual trajectories, there could be errors caused by improper rescaling the kinetic energy during a surface hop.