

# Implementation of global switching algorithm for trajectory surface hopping molecular dynamics in Newton-X package and benchmark performance on the Cis $\leftrightarrow$ trans azobenzene photoisomerization

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## Abstract

Newly developed global switching algorithm<sup>[1]</sup> that does not require calculation of nonadiabatic coupling vector reduces computational cost significantly and now is coded into Newton-X program package<sup>[2]</sup> with interfaces to various quantum chemistry program. However, there is a lack of extensive checking its accuracy for this simplest nonadiabatic molecular dynamic method in comparison with conventional Tully's fewest switches. It is very necessary to demonstrate how accurate global switching algorithm is. Extensive comparison between local and global switching on-the-fly trajectory surface hopping molecular dynamics (TSH-MD) is performed for cis-to-trans (800 sampling trajectories) and trans-to-cis (600 sampling trajectories) azobenzene photoisomerization at the OM2/MRCI level. Excellent agreement between two switching algorithms is obtained not only for highly averaged quantities of quantum yields and lifetimes, but also for detailed contour patterns of product distributions, hopping spot distributions and hopping directions in terms of conical intersections between ground and the first excited states. Moreover, the local and global switching TSH-MD is also performed for cis-to-trans (300 sampling trajectories) and trans-to-cis (300 sampling trajectories) azobenzene photoisomerization at Spin-flip DFT (SFDFT) level. The quantum yields, lifetimes and the hopping spot distributions simulated by the global switching TSH-MD at SFDFT level excellently agreed with previous theoretical values at CASSCF level and showed better performance than those by semiempirical OM2/MRCI method, while the local switching TSH demonstrated poor performance on the quantum yields of products due to lack of the analytical nonadiabatic coupling vectors determining the hopping directions at SFDFT level. Therefore, the global switching TSH-MD can be applied to larger complex systems where analytical nonadiabatic coupling is not available for excited-state molecular dynamic simulation.

**Keywords:** Global Switching, Surface Hopping, Newton-X, Azobenzene Photoisomerization

## References

- [1] Yu, L.; Xu, C.; Lei, Y.; Zhu, C.; Wen, Z. *Physical Chemistry Chemical Physics*. **16**, 25883 (2014).
- [2] M. Barbatti, G. Granucci, M. Ruckebauer, F. Plasser, J. Pittner, M. Persico and H. Lischka, NEWTON-X: a package for Newtonian dynamics close to the crossing seam, version 1.4, [www.newtonx.org](http://www.newtonx.org). (2013).