# VISTA Seminar

## Seminar 50

**April 26, 2023**

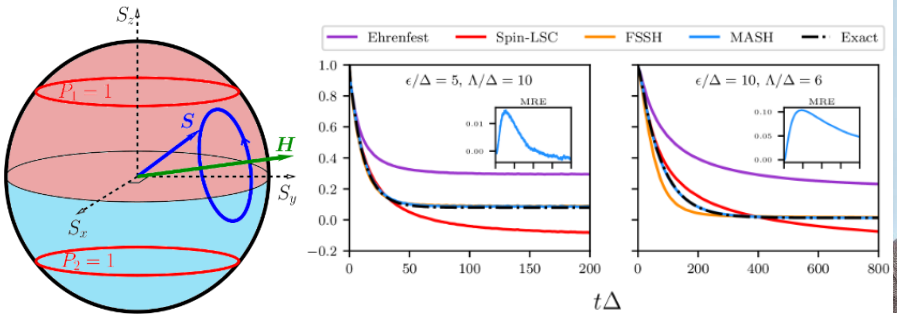
**10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT London / 4:00 pm – 5:30 pm CET Paris / 11 pm CST Beijing**

**TOC:**

# A Mapping Approach to Surface Hopping

Jeremy O. Richardson

*Laboratory of Physical Chemistry, ETH Zurich, Switzerland*
*Email: jeremy.richardson@phys.chem.ethz.ch*




We combine the best aspects of the two rivial nonadiabatic approaches of fewest-switches surface hopping (FSSH) and quasiclassical mapping methods to derive the Mapping Approach to Surface Hopping (MASH). Like quasiclassical mapping, MASH is rigorously derivable from the quantum-classical Liouville equation. Like surface hopping, MASH transitions between adiabatic surfaces, meaning that it recovers wavepacket branching and never moves on inverted potentials. Because of its rigorous derivation, it gives unique prescriptions for the momentum rescalings and decoherence corrections, which have proven to be controversial aspects of the standard FSSH approach. MASH trajectories evolve under fully deterministic equations of motion, which unlike FSSH, guarantees that there is always internal consistency between the active propagation surface and the time-evolved electronic state.

We show that MASH exhibits improved accuracy over FSSH in various model systems and in particular can recover Marcus theory without decoherence corrections. Given the current popularity of using FSSH in ab initio simulations of chemical systems, our new algorithm has the potential for offering a more accurate and rigorous dynamical method for these applications, all at a comparable computational cost.

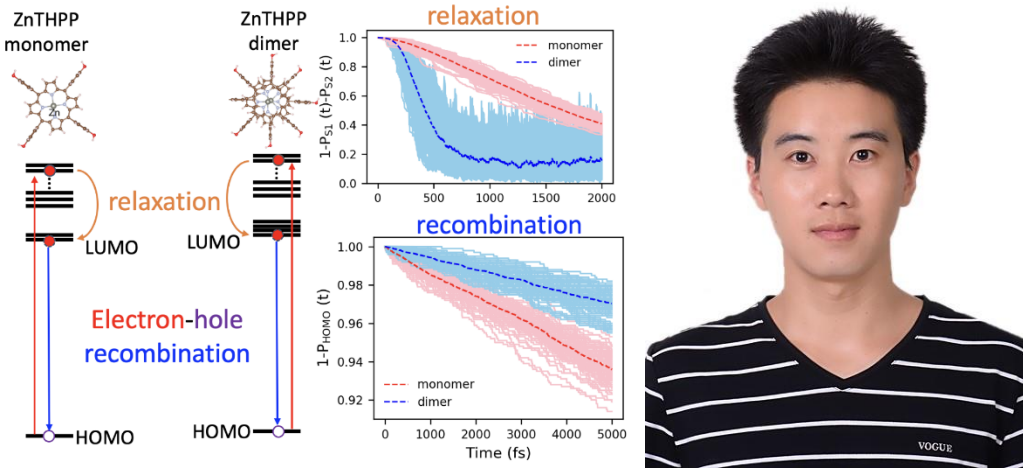
## References

[1] Johan Runeson and Jeremy Richardson, *JCP* **151**, 044119 (2019).
[2] Jonathan Mannouch and Jeremy Richardson, *JCP* **158**, 104111 (2023).

# Insight into the Molecular Mechanism for Longevity of Supramolecular Vesicular Photocatalysts

Fulu Zheng

*Bremen Center for Computational Materials Science, University of Bremen*
*Am Fallturm 1, Bremen 28359, Germany.*
*Email: fzheng@uni-bremen.de*




Supramolecular self-assembly is a promising strategy for stabilizing the photo-sensitive components in photocatalysis. However, the underlying correlation between the enhanced photostability and supramolecular structure at the molecular level has not yet been fully understood. Inspired by the supramolecular membrane in natural photosynthetic systems, a vesicular membrane-based photocatalyst is designed and synthesized recently, exhibiting highly stable photocatalytic hydrogen generation with at least activity time of 240 h under irradiation. Time-domain *ab initio* modelling is creatively introduced to unveil the physical mechanism underlying the excellent performance of the designed photocatalyst. It is found that the supramolecular aggregation does not only facilitates "hot" electron relaxation to offer high stability, but also prolongs the photo-generated carrier lifetime to promote charge separation. This work deepens the molecular-level understanding of photo-induced carrier dynamics in supramolecular structure, providing guidance of advanced photocatalyst design.

## References

[1] Y. Liu, F. Zheng, H. Dai, C. Chen, Y. Chen, H. Wu, C. Yu, Y. Mai, T. Frauenheim, Y. Zhou, Insight into the Molecular Mechanism for Enhanced Longevity of Supramolecular Vesicular Photocatalysts. *Angew. Chem. Int. Ed.* e202302126 (2023)

# How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 50
Time: Apr 26, 2023 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting
https://buffalo.zoom.us/j/95037727720?pwd=TktWbUkvMWZrd09EMVlxYlluVDFzZz09

Meeting ID: 950 3772 7720
Passcode: 253982