VISTA Seminar

Seminar 4

9:30 – 11:00 am EDT / 1:30 – 3:00 pm GMT

TOC:

Fragment orbital-based surface hopping (FOB-SH): Method, Implementation and Application

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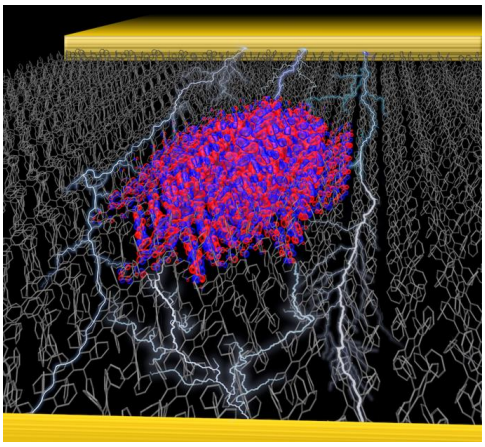

TOC: Snapshot of a flickering hole polaron in rubrene from FOB-SH simulation at 300K [10]

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Abstract: The combination of mixed quantum-classical non-adiabatic dynamics (MQC-NAMD) with time-dependent density functional theory (TDDFT) has proven to offer a powerful approach for the study of the photophysics and chemistry at the molecular scale. However, there are a host of important non-adiabatic problems that occur on larger length scales (> 5 nm) where this approach becomes computationally too expensive: charge and exciton transport and exciton dissociation in solar cell materials are prominent examples. Since these processes generally involve delocalized states QM/MM approaches are of not much help either. One possible way forward is to coarse grain the electronic structure and carry out the coupled electron-nuclear dynamics of the full system in a basis of local excitonic electronic states parametrized to explicit electronic structure calculations.[1-5] Our group has recently developed such a methodology in combination with fewest switches surface hopping that we dubbed fragment orbital-based surface hopping (FOB-SH), which I will present in my talk[5-8]. I will show that in large condensed phase systems improvements to Tully's original fewest switches surface hopping algorithm, are absolutely crucial for success: these are decoherence correction and treatment of decoherence-correction induced spurious long-range charge transfer as well as trivial crossing detection between the dense manifold of electronic states in the condensed phase[6-8]. I will also show how we could speed-up our original implementation at virtual no loss in accuracy to enable FOB-SH simulation of charge transport in very large molecular systems of more than 1000 organic molecules (~100,000 atoms), as required to reach convergence in the most conductive systems. Finally I will present how FOB-SH afforded a new physical picture of charge transport in high mobility organic materials: charge carriers (holes or excess electrons) form flickering polarons – highly dynamic quantum objects delocalized over many molecules but finite in size due to thermal disorder, see TOC graphic [9-10]. I will close with a brief overview over currently ongoing extensions of FOB-SH to exciton transport and exciton dissociation at truly nano-scale donor-acceptor interfaces.

References:

[1] A. Sisto, D. R. Glowacki, T. J. Martinez, ``Ab Initio Nonadiabatic Dynamics of Multichromophore Complexes: A Scalable Graphical-Processing-Unit-Accelerated Exciton Framework", *Acc. Chem. Res.* 47, 2857, 2014.

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[3] B. Smith, A. V. Akimov, ``Modeling non-adiabatic dynamics in condensed matter materials: some recent advances and applications", *J. Phys: Condens. Matter* 32, 073001, 2019.

[4] T. Kubar, M. Elstner, ``Efficient algorithms for the simulation of non-adiabatic electron transfer in complex molecular systems: application to DNA", *Phys. Chem. Chem. Phys* 15, 5794, 2013.

[5] J. Spencer, F. Gajdos, and J. Blumberger, "FOB-SH: Fragment orbital-based surface hopping for charge carrier transport in organic and biological molecules and materials," *J. Chem. Phys.* 145, 64102, 2016.

[6] A. Carof, S. Giannini, and J. Blumberger, "Detailed balance, internal consistency and energy conservation in fragment orbital-based surface hopping," *J. Chem. Phys.* 147, 214113, 2017.

[7] S. Giannini, A. Carof, and J. Blumberger, "Crossover from hopping to band-like charge transport in an organic semiconductor model: Atomistic non-adiabatic molecular dynamics simulation ," *J. Phys. Chem. Lett* 9, 3116, 2018.

[8] A. Carof, S. Giannini, and J. Blumberger, "How to calculate charge mobility in molecular materials from surface hopping non-adiabatic molecular dynamics – beyond the hopping/band paradigm," *Phys. Chem. Chem. Phys.* 21, 26368, 2019.

[9] S. Giannini, A. Carof, M. Ellis, H. Yang, O. G. Ziogos, S. Ghosh, and J. Blumberger, "Quantum localization and delocalization of charge carriers in organic semiconducting crystals," *Nature Comm.* 10, 3843, 2019.

[10] S. Giannini, O. G. Ziogos, A. Carof, M. Ellis, and J. Blumberger, "Flickering polarons extending over ten nanometers mediate charge transport in high-mobility organic crystals" *Adv. Theory Simul.* 3, 2000093, 2020.

Tully models revisited: The molecule is the limit?

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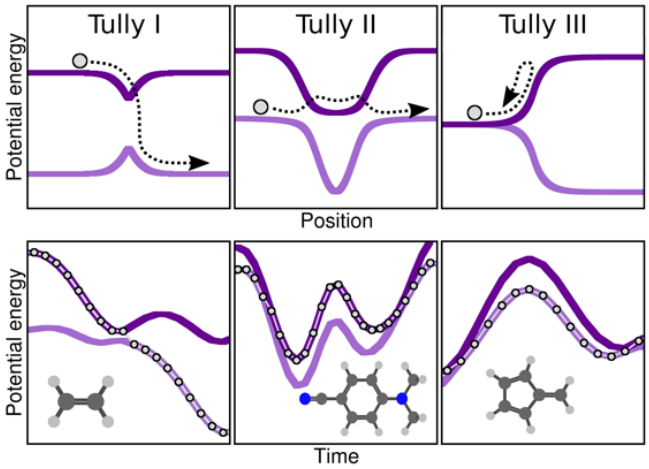

Abstract: Investigating the dynamics of photoexcited molecules usually involves overcoming the obstacles that arise due to the breakdown of the Born-Oppenheimer approximation. Over the last decades, a substantial number of methods have been developed to this end, using different ways to approximate the dynamics arising from the time-dependent molecular Schrödinger equation [1]. As all methods employ some inherent approximations, it is essential to carefully test them and determine the limitations imposed. To this end, in 1990, Tully proposed a series of three one-dimensional model systems used to test the approximations of the method called trajectory surface hopping [2]. The so-called Tully models aim to probe different processes observed during typical nonadiabatic dynamics: single nonadiabatic crossing, dual avoided crossing and reflection. These one-dimensional models have since arisen to a testbed for any new nonadiabatic dynamics strategy.

However, as nonadiabatic dynamics methods are usually employed to describe molecules in higher or full dimensionality, we may wonder, how representative Tully's one-dimensional models are of processes that molecules can undergo in their nonradiative deactivation. In this work, we present a molecular perspective to the Tully models by linking the simple one-dimensional models to processes occurring during the excited-state dynamics of molecules [3]. We not only give an abstract molecular interpretation of the original models, but also connect known nonadiabatic processes to a specific, exemplary molecule. As a result, we propose three molecules that could be used as molecular Tully models, reproducing some distinct features of the original models in a high-dimensional space. For the three molecular examples - ethylene, DMABN and fulvene – we (i) compare trajectory surface hopping with ab initio multiple spawning, (ii) highlight the key differences between the methods and (iii) dissect them to point to the distinct influences of their respective approximations.

The main focus of this work is to offer a molecular perspective on the original Tully models and a series of molecular tests for nonadiabatic dynamics methods. To this end, all the initial conditions for the models discussed are made available (DOI:10.15128/r1qj72p715m), so that they can be used as a unified mean of comparison for nonadiabatic molecular dynamics methods.

[1] L.M. Ibele et al., "Excited-state dynamics of molecules with classically driven trajectories and Gaussians", *Mol. Phys.* (**2020**), 118(8), e1665199
[2] J.C. Tully, "Molecular dynamics with electronic transitions", *J. Chem. Phys.* (**1990**), 93, 1061-1071
[3] L.M. Ibele and B.F.E. Curchod, "A molecular perspective on Tully models for nonadiabatic dynamics", *Phys. Chem. Chem. Phys* (**2020**), 22, 15183-15196

How to connect

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