VISTA

VISTA Seminar

Seminar 27

November 11, 2021

10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT / 4:00 pm – 5:30 pm Paris
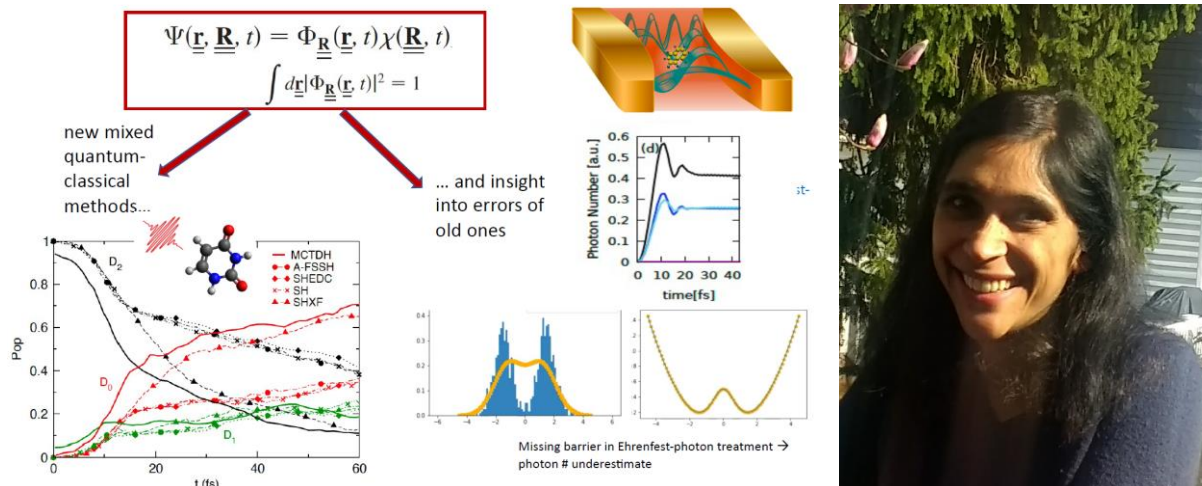
TOC:

Exact Factorization Adventures for Electrons, Nuclei, and Photons.

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The Exact Factorization (XF) approach offers a new perspective into the dynamics of coupled quantum subsystems. Writing the exact time-dependent wavefunction of the complete system as a single correlated product, one obtains evolution equations for each subsystem in which the potentials exactly contain the coupling to the other subsystems, enabling rigorous definitions of forces in mixed quantum-classical approximations. We discuss developments in two directions, one which highlights its practical significance, and the other demonstrates its use as an analytical tool. In the first, we consider non-adiabatic dynamics in a molecule with the XF-based surface-hopping method, SHXF developed by Seung-Kyu Min and co-workers Ha and Lee in 2018. The equation for the electronic coefficients contains a term that couples electronic states via the quantum momentum, which is crucial to accurately capture non-adiabatic dynamics and gives a first-principles description of decoherence. It plays an especially important role when more than two-states are occupied at any given time: we show that due to the lack of this term, traditional surface-hopping methods, including those with decoherence-corrections, fail to predict the dynamics accurately through a three-state intersection in the uracil cation, while SHXF performs similarly to the MCTDH benchmark. In the second direction, we step into the burgeoning field of polaritonic chemistry, where strong light-matter coupling due to confinement opens new possibilities for the manipulation of molecular landscapes. Here we extend XF to include photons as well, with different choices of factorizing emphasizing different aspects of the strong light-matter coupling. Features of the cavity-modified time-dependent potential energy surface directly correlate with suppression of proton-coupled electron-transfer, in contrast to polaritonic surfaces. The structure of the exact potential driving the photon dynamics identifies the cause of the underestimation of the photon number in multi-trajectory Ehrenfest treatments of the photon dynamics seen in recent studies.

Ab Initio Multiple Spawning with Informed Stochastic Selections

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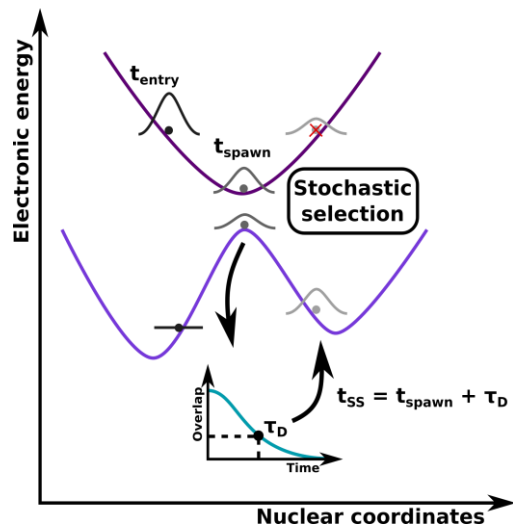
Ab-initio multiple spawning (AIMS) is a computational method for simulating the nonadiabatic dynamics of photoexcited molecules.[1] It uses an adaptable basis set of *coupled* travelling frozen Gaussians to represent the nuclear wavefunctions - making it an in principle exact method.[2] The frozen Gaussians, also known as trajectory basis functions (TBFs), are propagated classically on their corresponding adiabatic state. AIMS deals with nonadiabatic events by allowing its basis set to grow via the titular spawning process. Thus, whenever a TBF encounters a region of high nonadiabaticity, it will be able to make a copy of itself onto the coupled state. However, in some cases, the basis set may grow uncontrollably, leading to a considerable drop in efficiency. To stymie such unrestrained growth, the stochastically selected variant of AIMS (SSAIMS) was developed.[3] Within this approach, as soon as groups of TBFs separate in phase space, one group is randomly chosen to continue the dynamics, while the remaining TBFs are removed from the simulation. This talk will focus on the efficiency gained by introducing the stochastic selection idea[4] and present a new way of performing stochastic selection that does not resort to user-defined selection parameters. This so-called AIMS with informed stochastic selections (AIMSWISS) method[5] takes inspiration from the Schwartz decoherence correction to trajectory surface hopping[6]. Consequently, AIMSWISS will be shown to be a good compromise between efficiency and accuracy. This new development is likely to widen the range of application of the multiple spawning framework and make for an easier benchmark of more approximate methods.

References

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Topic: VISTA, Seminar 27
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