VISTA Seminar

Seminar 9

9:30 – 11:00 am EST / 2:30 – 4:00 pm GMT / 3:30 pm – 5:00 pm Paris

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The exact factorization: A predictive first-principles approach to non-adiabatic dynamics

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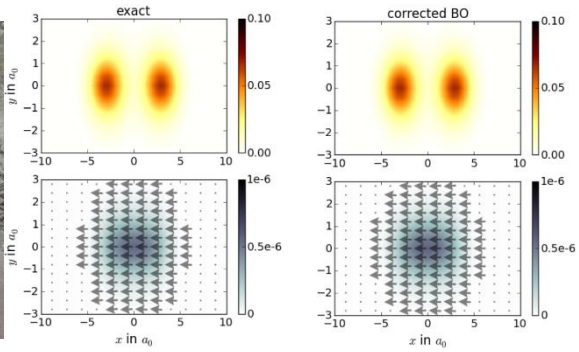

Some of the most fascinating phenomena in physics and chemistry, such as the process of vision, the dynamics of excitons in photovoltaic systems and the Nobel-prize-winning femto-chemistry experiments of Ahmed Zewail, occur in a regime where the coupled motion of electrons and nuclei beyond the adiabatic approximation is essential. The adiabatic approximation is among the most fundamental components in modern quantum chemistry and condensed-matter theory. It not only makes computations feasible, it also provides us with an intuitive picture of many chemical reactions. Yet it is an approximation. To go beyond it is notoriously difficult because one has to start from the full many-body Hamiltonian of interacting electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these two wave functions provide an ideal starting point to develop efficient algorithms for the study non-adiabatic phenomena. The successful prediction of laser-induced isomerization processes [2], the description of decoherence [2,3], calculations of the molecular Berry phase without invoking the Born-Oppenheimer approximation [4], evaluation of electronic currents [5] associated with nuclear motion and accurate predictions of vibrational spectroscopies [6], especially dichroism [7], will demonstrate the power of this new approach. To tackle non-adiabatic phenomena in solids, such as laser-induced phase transitions, the equations of motion of the exact factorization are "density-functionalized" [8], leading to a coupled set of Kohn-Sham equations for electrons and phonons [9].

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[6] A. Scherrer, F. Agostini, D. Sebastiani, E.K.U. Gross, R. Vuilleumier, *Phys Rev X* **7**, 031035, (2017).
[7] A. Scherrer, F. Agostini, D. Sebastiani, E.K.U. Gross, R. Vuilleumier, *JCP* **143**, 074106 (2015).
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[9] R. Requist, C.R. Proetto, E.K.U. Gross, *Phys Rev B* **99**, 165136 (2019).

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Trajectory surface hopping for nonadiabatic dynamics of resonances

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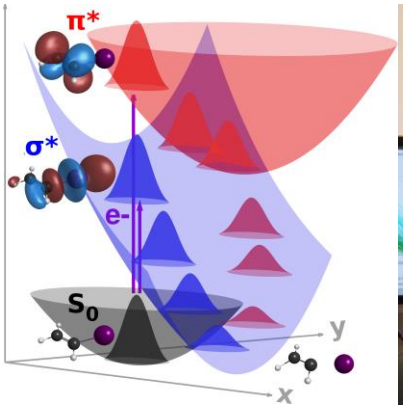

Abstract: There are a multitude of methodologies for describing nonadiabatic molecular dynamics of closed systems, comprising a set of discrete (localized) electronic states. However, there is a lack of approaches when couplings to a continuum (delocalized) of scattering states take place, *i.e.*, when the total population of the discrete part is not conserved. Current approaches rely on building potential energy surfaces of reduced dimensionality, which hinders their applicability to more involving and realistic multidimensional problems. Here, I'll present our recently proposed methodology [1] for describing the nonadiabatic dynamics of systems that can decay via an external mechanism. The complex surface fewest switches surface hopping (CS-FSSH) method can be seen as a generalization of the standard trajectory surface hopping [2] to the case of complex-valued potential energy surfaces, or as a generalization of a previous approach for adiabatic dynamics of decaying states [3]. Benchmarks against exact quantum dynamics results for model problems demonstrate the validity and limitations of the methodology. As a first application, we have considered the relaxation of iodoethene transient anions, as formed by resonant electron attachment. We have provided the first detailed and dynamical picture of the π*/σ* mechanism of dissociative electron attachment in halogenated unsaturated compounds, which is believed to underlie electron-induced reactions of several molecules of interest [4]. The CS-FSSH methodology allows for arbitrary decaying mechanisms to be included via imaginary potentials. It is therefore not limited to the case of transient anions, and some other interesting possibilities will be discussed.

References

[1] F. Kossoski, M. Barbatti, "Nonadiabatic dynamics in multidimensional complex potential energy surfaces", *Chem. Sci.* 11, 9827 (2020).
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