VISTA Seminar

Seminar 6

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

TOC:

Coherent photoexcited dynamics and intermolecular conical intersections

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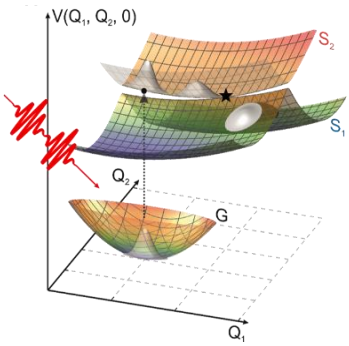

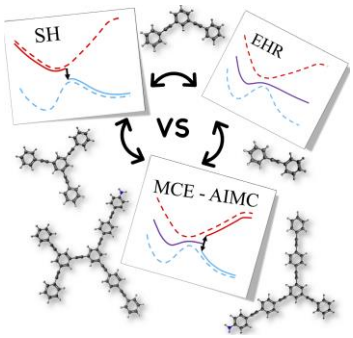

In this talk, I will overview some applications of semiempirical Non-adiabatic EXcited-state Molecular Dynamics (NEXMD) framework developed at several institutions and recently released to public. The NEXMD code is able to simulate tens of picoseconds photoinduced dynamics in large molecular systems with hundreds of atoms in size and dense manifold of interacting and crossing excited states. A variety of implemented non-adiabatic dynamics algorithms (including surface hopping, Ehrenfest, and ab initio multiple cloning) permits the flexibility of choosing the right approximation with respect to numerical cost. In particular, I will exemplify ultrafast coherent excitonic dynamics guided by *intermolecular* conical intersections (CoIns). Both simulations and time-resolved two-dimensional electronic spectroscopy track the coherent motion of a vibronic wave packet passing through CoIns within 40 fs, a process that governs the ultrafast energy transfer dynamics in molecular aggregates. Our results suggest that intermolecular CoIns may effectively steer energy pathways in functional nanostructures. In the second example, we use non-adiabatic excited state dynamical simulations to compute X-ray Raman signals, which are able to sensitively monitor the coherence evolution in a rigid synthetic heterodimer. The observed coherences have vibronic nature that survives multiple conical intersection passages for several hundred femtoseconds at room temperature. These spectroscopic signals are possible to measure at XFEL facilities, paving the way for detailed coherence measurements in functional organic materials. Observed relationships between spatial extent/properties of electronic wavefunctions and resulting electronic functionalities allow us to understand and potentially manipulate excited state dynamics and energy transfer pathways toward optoelectronic applications.

Relevant references

1. T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, *"Non-adiabatic Excited-State Molecular Dynamics: Theory and Applications for Modeling Photophysics in Extended Molecular Materials"* Chem. Rev. **120**, 2215 (2020)
2. W. Malone, B. Nebgen, A. White, Y. Zhang, H. Song, J. Bjorgaard, A. Sifain, B. Rodriguez-Hernandez, S. Fernandez-Alberti, A. E. Roitberg, T. Nelson and S. Tretiak, *"NEXMD Software Package for Non-adiabatic Excited State Molecular Dynamics Simulations"* J. Chem. Theory Comput. **16**, 5771 – 5783 (2020).
3. T. R. Nelson, D. Ondarse-Alvarez, N. Oldani, B. Rodriguez-Hernandez, L. Alfonso-Hernandez, J. F. Galindo, V. D. Kleiman, S. Fernandez-Alberti, A. E. Roitberg, S. Tretiak, *"Coherent Exciton-Vibrational Dynamics and Energy Transfer in Conjugated Organics"* Nature Comm., **9**, 2316 (2018).
4. A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A. Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, *"Intermolecular conical intersections in molecular aggregates"* Nature Nanotech. (2020, https://doi.org/10.1038/s41565-020-00791-2).

Surprisal of a quantum state: dynamics, compact representation and coherence effects

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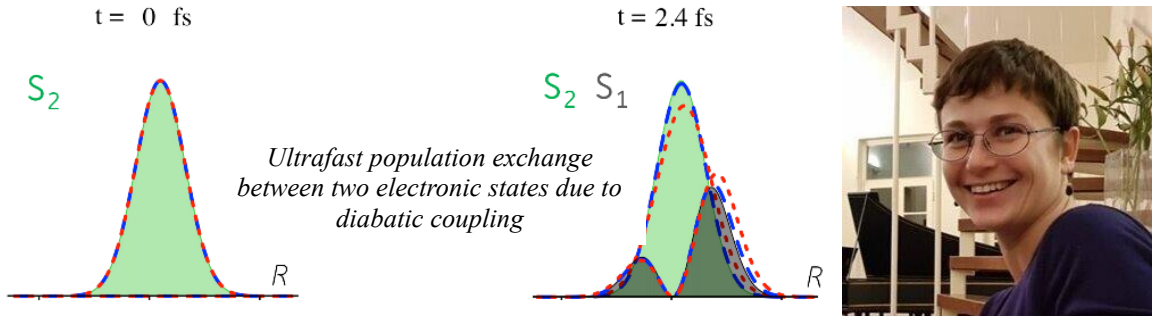

The state of a quantum mechanical system, pure or mixed, is described by a density operator. Surprisal – the logarithm of the density matrix – follows the same unitary evolution as the density operator. The maximal entropy formalism provides an explicit form of the density as an exponential function of a set of operators, whose observables are given. It allows to describe the state of the system explicitly via our knowledge about its observables [1-4]. The most well-known example of such a function is Boltzmann distribution, $\hat{\rho} = Z^{-1}\exp\{-\beta\hat{H}\}$, where the state of the system is defined by only one observable – energy. In general, there can be more than one operator that contributes to the density and these operators do not necessarily commute. Hence, the representation of the surprisal, logarithm of the exponential function, is a simpler construct then the density itself and allows more compact description of a quantum state.

To illustrate the idea, I will focus on a most simple example of a non-adiabatic dynamics – non-radiative decay between two electronic states due to diabatic coupling, modeled after pyrazine [5, 6]. In this example electronic and nuclear degrees of freedom are coupled and coherence effects are prominent.

TOC description: The wavepacket density on the upper electronic state is plotted in light green, and in dark grey on the lower electronic state as a function of normal mode nuclear coordinate, *R*. The panels are computed for increasing time values as indicated. Shown also are two approximate computations where the surprisal is expanded in a minimal basis of dominant constraints $\left\{I_N, \hat{a}, \hat{a}^\dagger, \hat{a}^\dagger\hat{a}\right\}$, red dotted curve, and in the extended set $\left\{I_N, \hat{a}, \hat{a}^\dagger, \hat{a}^2, (\hat{a}^\dagger)^2\hat{a}^\dagger\hat{a}\right\}$, blue dashed curve.

References

[1] E. T. Jaynes, "Information Theory and Statistical Mechanics," Phys. Rev. **106**, 620 (1957).
[2] E. H. Wichmann, "Density Matrices Arising from Incomplete Measurements," J. Math. Phys. **4**, 884-896 (1963).
[3] R. D. Levine, "Information Theory Approach to Molecular Reaction Dynamics," Annu. Rev. Phys. Chem. **29**, 59 (1978).
[4] Y. Alhassid and R. D. Levine, "Connection between the maximal entropy and the scattering theoretic analyses of collision processes," Phys. Rev. A **18**, 89 (1978).
[5] R. Schneider, W. Domcke. S_1-S_2 Conical intersection and ultrafast S_2 -> S_1 internal conversion in pyrazine. Chem. Phys. Lett. 150, 235 (1988).
[6] K. Komarova, F. Remacle, R.D. Levine. Surprisal of a Quantum State: Dynamics, Compact Representation and Coherence Effects. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.12981857.v1

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Alexey Akimov is inviting you to a scheduled Zoom meeting.

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