

# VISTA Seminar

## Seminar 7

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

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## Traveling in a space of approximations for modeling of photoinduced dynamic processes

Dmitri Kilin

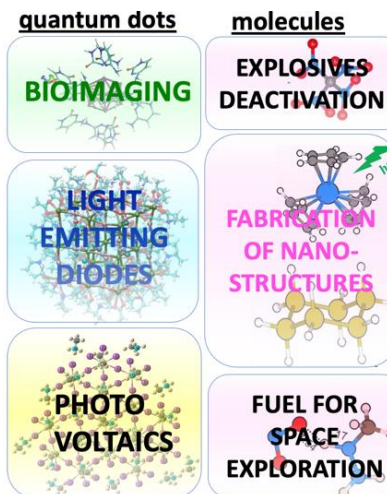
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Computational modeling of basic photoinduced processes helps to interpret and predict outcome of a broad range of experiments for characterization of molecules and nanomaterials. The talk focuses on approximations in computational methodology, needed for identifying mechanisms of the common photoinduced processes: (i) photoluminescence and (ii) photoreactions. (i) An approach combining the non-adiabatic time-domain DFT with the time-dependent density matrix technique,



allows one to identify conditions affecting radiative and nonradiative spin-allowed and spin-forbidden energy pathways and simulate emission spectra for newly designed structures with complicated surface chemistry.[1] This approach enables modeling of thermal linewidth broadening, transitions beyond Kasha's rule, and optical transitions with spin-flip, for systems that include transition metals and lanthanides.[2] Lineshape, linewidth, intensity, and quantum yield of photoluminescence[3] as well as down-conversion rates[4] have been predicted for a range of silicon, silver[5] and lead halide perovskite nanostructures[6]. Findings from this research direction promise benefits in applications to light emitting devices and biocompatible fluorescent sensors. Computed trends may contribute to novel design strategies of nanomaterials with improved functionalities critical for optoelectronic applications. (ii) An approximate computational procedure, based on Rabi oscillations, was used to model photochemical processes induced by mid-to-high intensity of laser irradiation. This procedure is verified by reproducing experimental mass spectra for photodecomposition of lanthanide metalorganic complexes[7] and explosive molecules.[8] This approach has been adapted for photo-polymerization reactions of cyclohexasilanes used in fabrication of Si nanostructures for electronics and photovoltaics.[9] Considered approximations and their range of applicability are expected to help in future modeling of systems where photophysical and photochemical processes occur simultaneously.



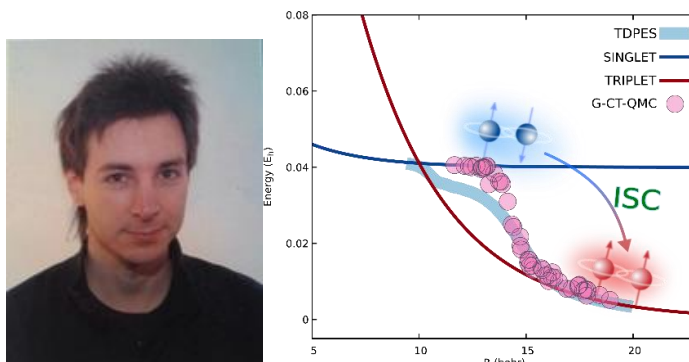
- [1] Jensen, et al., *J. Mater. Chem. C*, **2019**,7, 2625-2632.  
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 [4] Vogel, et al., *J. Phys. Chem. Lett.* **2017** 8, 3032-3039.  
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 [6] Forde et al., *J. Phys. Chem. C* **2020**, 124, 1, 1027–1041.  
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 [9] Han et al., *J. Phys. Chem. Lett.* **2018**, 9, 4349–4354.

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## HOW TO TREAT RADIATIONLESS TRANSITIONS WITH EXACT FACTORIZATION

Francesco Talotta

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Radiationless transitions are important non-adiabatic phenomena that take place in excited molecular systems. Depending on the type of electronic states involved and the type of state-to-state couplings, these transitions can be classified into internal conversions (ICs) and intersystem crossings (ISCs). The former involve states of the same spin multiplicity interacting via the non-adiabatic couplings (NACs), whereas the latter involve states of different spin multiplicity interacting via the relativistic spin-orbit couplings (SOCs).

A proper description of these non-radiative transitions is of utmost importance in the study of photophysical and photochemical properties of the molecular systems, as ICs and ISCs are notoriously responsible for ultrafast relaxations processes. Therefore, a number of computational methods have been developed in the last decades to simulate non-adiabatic dynamics with classical-like trajectories, such as the very popular trajectory surface hopping (SH) [1], or the novel coupled trajectory mixed quantum/classical (CT-MQC) method [2].

In my presentation, I will first briefly review the main ideas behind CT-MQC, pointing out the main features and current applicability of the method. Then, I will focus on the CT-MQC algorithm, on the latest development and extension of this method with the inclusion of the relativistic spin-orbit interactions, to let CT-MQC dealing with both NACs and SOC on the same footing [3,4]. A brief review of the theory and implementation of SOC in CT-MQC will be presented, together with a detailed assessment of the new algorithm, through application on simple 1D SOC model systems [5] that can be easily compared with the exact quantum wavepacket dynamics. The results of both CT-MQC and exact calculations will be critically discussed, underlining the very good agreement between the two methods, but also the limitations of the current implementation. A detailed explanation of the reasons behind this limitations will be also presented.

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[5] G. Granucci et al., *J. Chem. Phys.* **2012**, 137, 22A50.

### How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 7

Time: Dec 3, 2020 09:30 PM Eastern Time (US and Canada)

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