VISTA Seminar

Seminar 47

December 14, 2022

10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT London / 4:00 pm – 5:30 pm CET Paris / 11 pm CST Beijing

TOC:

Can we describe photochemistry without nonadiabatic dynamics?

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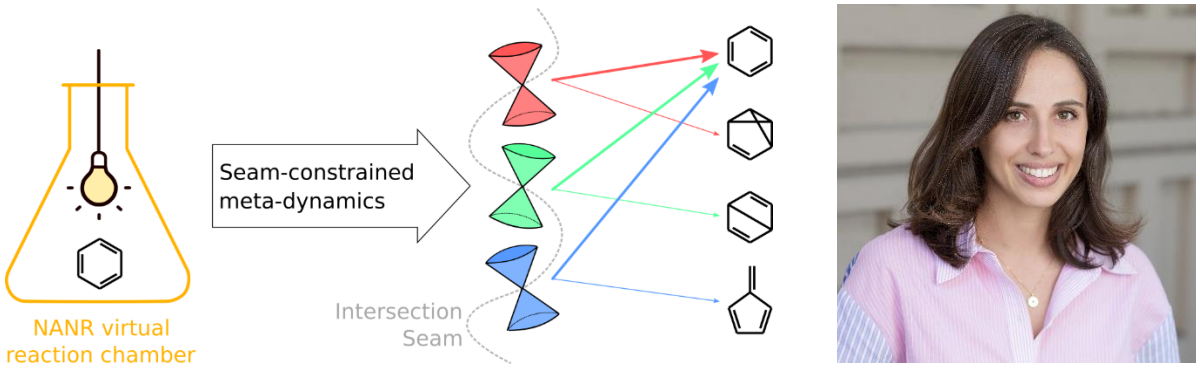

Successful attempts have been made in automated reaction discovery for ground state chemistry. However, automated photorection discovery represents a much bigger challenge due to a multiplicity of technical and conceptual issues (e.g., the lack of a comprehensive nonadiabatic transition state theory).

The recently developed Nonadiabatic Nanoreactor employs a new scheme to identify all the possible photoproducts of a photoreaction. We use seam-constrained metadynamics to extensively probe the intersection seam between two electronic states and identify representative conical intersections. Systematic sampling of the branching plane and subsequent relaxation on the ground state allows to find available photoproducts.

We show that a crude model achieves reasonable success in quantitatively estimating the branching ratios, and we discuss the impact of the limitations involved and strategies to overcome them.

Classification of Doubly Excited Molecular Electronic States

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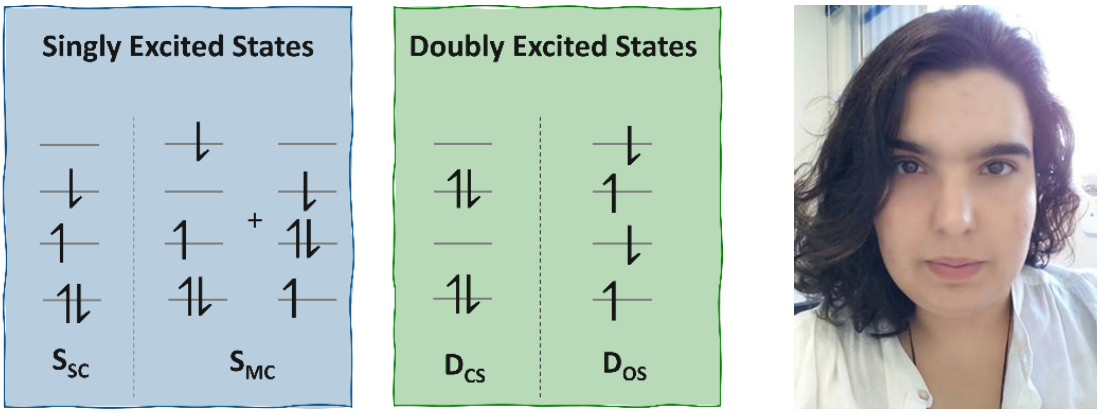

Electronic states with partial or full doubly excited characters play a crucial role in many areas, such as singlet fission and non-linear spectroscopy. Although doubly-excited states have been studied in polyenes and related systems for many years, their assignment as single vs. doubly excited, even in simple polyenes, such as butadiene, has sparked controversies. So far, no well-defined framework for classifying doubly excited states has been developed, and even more, there is not even a well-accepted definition of doubly excited character. Here, we present a solution: a physically motivated definition of doubly excited character based on operator expectation values and density matrices, which works independently of the underlying orbital representation, avoiding ambiguities plagued in earlier studies. Furthermore, we propose a classification scheme to differentiate two limiting cases: two single excitations occurring within two independent pairs of orbitals leaving four open shells (D_{OS}) and the promotion of both electrons to the same orbital, producing a closed-shell determinant (D_{CS}). We illustrate the conversion between those two limiting cases using a well-known photochemical reaction, ethylene dimerization. This work provides a deeper understanding of doubly excited states and may guide more rigorous discussions towards improving their computational description yet providing insight into their fundamental photophysics.

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 47
Time: Dec 14, 2022 10:00 AM Eastern Time (US and Canada)

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