Advances and Perspectives on Mixed Quantum-Classical Dynamics

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Electronically-excited molecular and supramolecular systems are central to diverse fields, including biology (photosynthesis, vision), health (phototherapy, imaging), and technology (photonics, photovoltaics, photocatalysis).

Upon photoexcitation, these molecules and molecular assemblies are unequilibrated systems, with multiple competing reaction pathways and time evolution spanning from few picoseconds to microseconds depending on the processes involved. Moreover, they present highly complex electronic densities and often visit geometric conformations with multireference character. Such features make their analysis challenging for both experimentalists and theoreticians, and the synergy between these fields has been the key to characterize these systems successfully.

Nonadiabatic mixed quantum-classical (NA-MQC) dynamics simulations [1], a subfield of computational chemistry of the excited states, helps by providing insights into the physical-chemical phenomenon, delivering information for the deconvolution of experimental time-resolved data, and predicting properties before and after synthesis. Using NA-MQC dynamics, however, faces different challenges, including the development of new functionalities, reliable research protocols, efficient computational methods, integration with experimental analysis, and balanced description of the electronic correlation between different diabatic states.

In this lecture, I will present applications showing how NA-MQC dynamics can be used to investigate electronically-activated organic systems. In particular, I will discuss how recent methodological advances in NA-MQC dynamics implemented by our and other groups have been pushing the field's boundaries towards more complex systems (large molecular aggregates), unexplored phenomena (intersystem crossing, tunneling, polaritonics, dissociative electron attachment), and more precise description of the dynamics evolution (super-exchange, decoherence, quantum delocalization).

Despite this vibrant surge of new algorithms, most of NA-MQC dynamics simulations bear a significant underlying flaw, the low accuracy of their predictions. This issue, which may even lead to qualitatively wrong assessments, is mainly caused by the downgrade of the electronic-structure levels, needed to cope with the high computational costs. I will critically appraise the field and examine new developments and perspectives that may improve the situation, including the advent of machine learning.

[1] Crespo-Otero, R.; Barbatti, M. Recent Advances and Perspectives on Nonadiabatic Mixed Quantum-Classical Dynamics. Chem. Rev. 2018, 118, 7026-7068.