How to treat radiationless transitions with exact factorization

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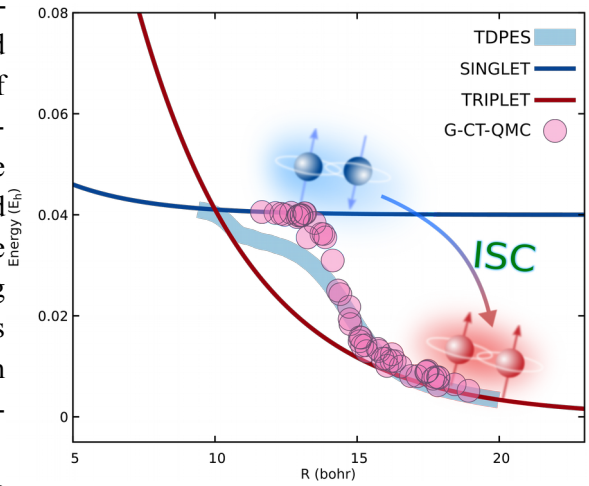
ABSTRACT

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 SOCs on the same footing [3,4]. A brief review of the theory and implementation of SOCs 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, underling 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.

References

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