New strategies for density functional calculations of excited states and application to ultrafast photoreactions in solution

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Simulating photochemical processes requires methods that can describe different types of electronic excitations and their nuclear energy surfaces. Variational density functional calculations where excited states are obtained as high energy solutions of the Kohn-Sham (KS) equations are emerging as a powerful tool. They have the same computational cost as ground state calculations, provide analytical atomic forces, and, thanks to state-specific orbital relaxation, can describe a broad range of excitations, including charge transfer, Rydberg and doubly excited states. Compared to the ground state, it is, however, more challenging to obtain excited state solutions. First, excited states typically correspond to saddle points on the multidimensional surface given by the variation of the energy as a function of many electronic degrees of freedom (the orbital rotations). Second, excited states often display degeneracies, which lead to convergence issues for common self-consistent field procedures based on eigensolvers.

The talk will illustrate the methodologies that we have developed for variational density functional calculations of excited states[1,2], which, instead of solving the KS eigenvalue problem, directly optimize the orbitals by finding the orbital rotations that make the energy stationary. In this way, the calculations can be tailored to converge to saddle points on the electronic energy surface. The methods employed include efficient quasi-Newton algorithms and a robust mode following approach generalized to target saddle points of any order. The new methodologies made it possible to explore energy surfaces close to conical intersections and avoided crossings[3], and to assess the performance of semilocal functionals on charge transfer excitations in organic molecules. We further use the direct optimization methods in multiscale molecular dynamics simulations of the photochemical dynamics of solvated molecules to aid the interpretation of time-resolved X-ray scattering experiments performed at large scale synchrotron and X-ray free electron laser facilities. As an example, the talk will show how the simulations made it possible to elucidate the rearrangement of the solvent following photoexcitation of a copper photosensitizer and how it influences the ligand dynamics and photosensitizing properties of the complex[4].

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