Dynamics and control of open quantum systems:
The example of a Cope rearrangement

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The study of quantum coherences and their exploitation for control by laser pulse is still a numerical challenge in big systems. Several strategies coexist and complement one another. The method we present here focuses on a quantum subspace that is coupled to a dissipative thermal bath described by a spectral density. We adopt a non-markovian master equation for the evolution of the density matrix of the quantum system. This approach, proposed by Meier and Tannor [1,2], is perturbative in the system-bath coupling but not in the interaction with a laser field. It has the advantage of being valid for any timescales that occur in the system dynamics or in the bath relaxation. It leads to a coupled equation system between the system density matrix and auxiliary matrices that depend on the setting of the correlation function of the bath of oscillators. Our goal is to confront this methodology to systems calibrated by *ab initio* calculations.

One of our applications is the control of a Cope rearrangement, in the context of Diels-Alder reactions. The dimerization of methyl-cyclopentadienylcarboxylate predominantly leads to Thiele's ester, and we try to optimize a field leading to a stable isomer via the Cope transition state.
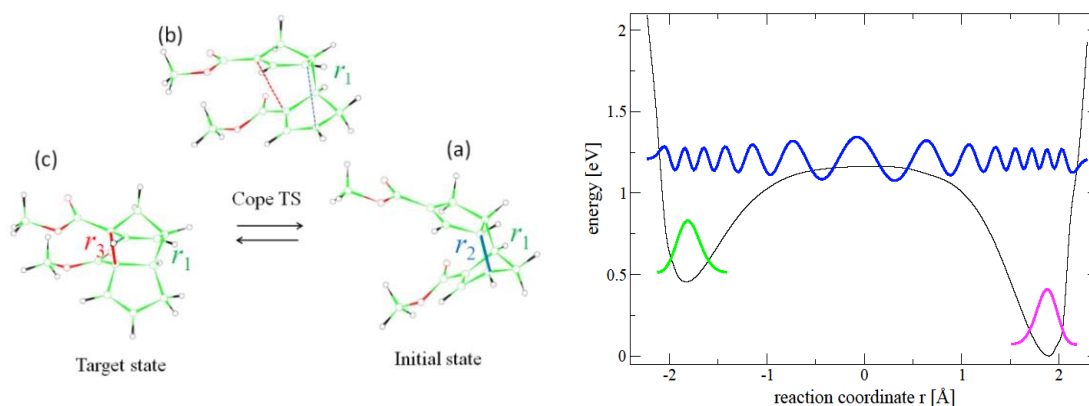
We combine the quantum dynamical approach described above with the optimal control theory (OCT) method [3]. We construct optimal fields in the presence of dissipation. We show that including the dissipation at the design stage of the field enables the control algorithm to react on the environment-induced decoherence and to find a way different from the one found without bath, with a better yield, through the delocalized quantum states placed above the potential barrier [4,5].

References:
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