Full dimensional quantum description (48D) of the ring-opening dynamics of benzopyran through a conical intersection with ML-MCTDH

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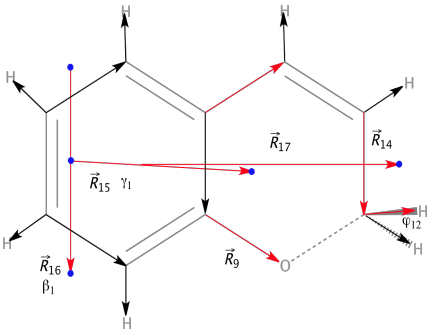
Modern challenges in theoretical chemistry concern the extension of studies of dynamics and control to larger molecules in a complex environment such as protein, a solvent, a matrix, etc[1]. We focus on photochemical mechanisms in organic compounds where conical intersections (CI) play a major role, more specifically on the ring-opening reaction for spiropyran molecules and their chromophore, benzopyran (see Figure) molecules. This formidable task, so far little studied, requires the development of innovative approaches combining sophisticated models of quantum chemistry and the use of very recent programs for quantum dynamics.

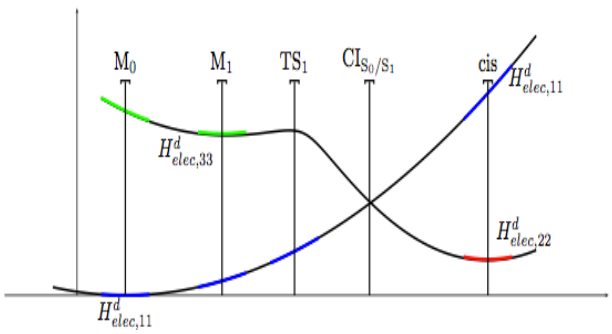
The two main challenges in treating large molecular systems with a full quantum-mechanical approach are

(i) Generating the potential energy surfaces as fitted analytical functions of the nuclear coordinates (see Figure)[2]

For this task, the main idea is the following. We assume that the set of 9 active coordinates is sufficient to describe the reaction leading from the Franck-Condon geometry to the conical intersection, and we add the effect of other coordinates using a harmonic approximation.[2,3]

(ii) Solving the Time Dependent Schrödinger equation for the nuclei for 48 degrees of freedom. This is achieve with the Multi-Layer Multi-configuration Time depend Hartree method (ML-MCTDH)[4,5].





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