Theoretical design of conical intersections in molecular motors and switches: A Density Functional Theory perspective

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It is widely recognized that conical intersections (CIs) play the dominant role for the mechanism of photochemical reactions providing very efficient funnels for radiationless relaxation processes [1]. For designing new types of photoactive molecules, such as molecular motors and switches [2], a deep understanding of the factors affecting the occurrence of CIs and the respective molecular geometries of the reactive species is needed [3]. In the present work, a computational method based on ensemble density functional theory, the spin-restricted ensemble-referenced Kohn-Sham (REKS) method [4], will be used to investigate CIs in a wide range of organic molecules and chromophores of photoactive proteins [5]. By comparing the geometries of the minimum energy CIs (MECIs) obtained with the use of various density functionals, ranging from the global hybrid functionals to the local hybrid and to the meta GGA hybrid functionals, against the reference data from the ab initio multireference (MRCI, MS-CASPT2) calculations [5], the role of the density functional for obtaining accurate MECI molecular geometries and relative energies will be investigated. The influence of the relative electronegativity of the fragments connected by the double bond undergoing photoisomerization [6] on the MECI's geometry and topography will be studied and predictions regarding the rules for designing molecular motors and switches will be drawn. These design rules will be illustrated by application to novel molecular motors with improved functionality.

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