Explorative study of the singlet fission process

Remco W.A. Havenith, Hilde D. de Gier and Ria Broer

Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

The efficiency of converting sunlight into electricity can be improved by a process called singlet fission. Through singlet fission, or multiple exciton generation, two pairs of charge-carriers instead of one can be generated by one photon. Singlet fission is a radiationless process in which an excited singlet state, S_1, localized on one of a pair of neighbouring chromophores, is converted into another excited state that consists of two triplets, each on one of the two chromophores. These two localized triplets are coupled into an overall singlet state, often denoted ^{1}TT.

For efficient energy transfer from S_1 to ^{1}TT, their energies should be similar. For estimating the decay rate, two scenarios can be considered. The transfer can be driven by nuclear motion and then knowledge of the potential energy surfaces and vibrational frequencies is required, together with the non-adiabatic coupling elements between the states. On the other hand, for Dexter type transitions in which the two chromophores bilaterally exchange their electrons, estimates of the electronic coupling between the relevant local states need to be made.

With standard quantum chemical methods the energies of the relevant states can be well estimated, but non-adiabatic and electronic couplings between the local states are not easily accessible. In this presentation we show how these questions can be addressed using multi-reference methods CASSCF and CASCI, combined with second order perturbation theory and nonorthogonal CI, respectively. The approach is illustrated using a few examples. For 2-methyl-1,5-hexadiene a proof of principle is given for the calculation of a singlet fission pathway driven by nuclear motion. The nonorthogonal CI approach is used to investigate electronic couplings in a tetracene trimer. The role of charge transfer states as intermediates is also investigated.