Multistate multimode vibronic pathways of singlet fission: A DMRG's perspective

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Singlet fission (SF), one of the most promising processes that can potentially improve solar cell efficiency, downconverts the higher energy photons and allows photovoltaic devices to surpass the Shockley-Queisser limit. However, the relevant advancements in the SF research state two major limitations: (i) the mechanism of the SF process in organic molecules is poorly understood, and (ii) there are not many molecules fulfilling the SF criterion and undergoing the fission process. We develop an extensive wavefunction methodology based on Density Matrix Renormalization Group (DMRG) method to not only explain the mechanistic details of existing SF chromophores but also to pave a pathway for discovering new SF systems. The pioneering use of two-particle local spin descriptor and the consideration of vibronic couplings between multiple SF states of pentacene dimer indicates the role of two distinct charge-transfer states in different vibronic regions. The multimode vibronic interactions delocalize the exciton for a TT state via *out-of-phase* vibrational charge-transfer interactions allowing the formation of two distinct triplets along with a modified vibronic structure.

Although many polyacene crystals have shown outstanding SF performance, their instability remains an obstacle in realizing their potential in photovoltaic devices. We develop Azaborine stabilized potential SF candidates that satisfy the existing SF criterion. To enhance the SF performance, we modify the structural packings and find the local maxima of SF rates using Marcus theory. Our analysis highlights that the energetic criterion for monomers merely provides a guideline and it is molecular packing that can dictate the SF dynamics in many cases.

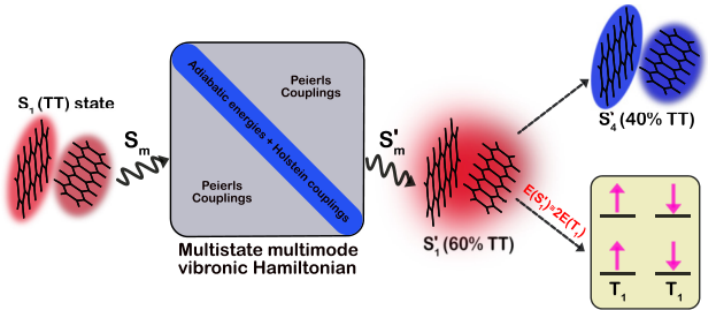

Figure. The vibronic Hamiltonian for singlet fission of pentacene includes five low-lying excited states of different electronic characters. The initial S_1 state eventually splits into two free triplets as a result of vibronic progression.

References

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