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Fission of Entangled Spins: An Electronic Structure Perspective XINTIAN FENG, Department of Chemistry, University of Southern California, Los Angeles, California, ANATOLIY LUZANOV, STC Institute for Single Crystals, National Academy of Sciences, Kharkov, Ukraine, ANNA KRYLOV, Department of Chemistry, University of Southern California, Los Angeles, California — Electronic structure aspects of singlet fission process are discussed. Correlated adiabatic wave functions of the bright singlet and dark multiexciton states of tetracene and pentacene dimers are analyzed in terms of their character (excitonic, charge-resonance, multiexciton). At short interfragment separation (3.5-4.0 angstroms), both multiexcitonic and singly-excited singlet states have noticeable charge-resonance contributions that fall off quickly at longer distances. Non-adiabatic couplings between the states are discussed. The limitations of diabatic framework in the context of singlet fission are explained. Based on the Cauchy-Schwarz inequality, we propose using the norm of one-particle transition density matrix, $||\gamma||$, as a proxy for couplings. The analysis of $||\gamma||$ and state characters reveals that the couplings between the multiexciton and singly-excited states depend strongly on the weights of charge-resonance configurations in these states. To characterize energetics relevant to triplets separation step, we consider multiexciton binding energy (E_b) defined as the difference between the quintet and singlet multiexciton states. The effect of fragment orientation on the couplings and E_b is analyzed.

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