

# Singlet Fission Couplings Calculated with Complete-Active-Space Self-Consistent Field (CASSCF) Theory

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Singlet fission (SF) has recently attracted much attention to its potential for drastic improvement of organic solar-cell efficiency. In this study, we have developed a method to calculate the electronic coupling for the SF at complete active space self-consistent field (CASSCF) level of theory. Our method is based on a diabaticization scheme consisting of the following two-step unitary transformations; the first one is carried out on the coefficients of the active orbitals to obtain the fragment molecular orbitals and the second one on the coefficients of Slater determinants in the CAS-configuration interaction (CAS-CI) space. The CASSCF calculations with the diabaticization scheme produce the Hamiltonian matrix in the diabatic states representation (which includes locally neutral excited states,  $^1(S_1S_0)$  and  $^1(S_0S_1)$ , charge-transfer ones,  $^1(CA)$  and  $^1(AC)$ , and multi-excited state  $^1(T_1T_1)$ ). The SF coupling is calculated with the super-exchange model or bridge Green function method, where the SF from  $^1(S_1S_0)$  to  $^1(T_1T_1)$  occurs via  $^1(CA)$  and  $^1(AC)$  as the virtual intermediate states in the perturbation theory.

We first apply our method to several configurations of a pentacene dimer in a crystal structure. We found that the Hamiltonian matrix obtained from our method is similar to that from the diabaticization scheme called four-fold way[1] in Ref. [2]. We then calculated the SF couplings of several oligoacenes dimers in their crystal structures. Our results reasonably agree with those reported in the previous works [3,4].

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[4] Yang, C.-H.; Hsu, C.-P. *J. Phys. Chem. Lett.* **2015**, *6*, 1925.