Characterization for Diabatic States for Singlet Fission Rates

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In the simulation of dynamics with curve-crossing, the states involved are close in energy, and the Born-Oppenheimer approximation breaks down. The dynamics is better described with diabatic states, which generally require additional conditions in their definition and description. Even though diabatic states are originally defined as the eigenstates of the kinetic energy operator, they are over-determined for systems with more than two atoms [1]. Thus, an alternative definition is necessary. Diabatic states are often defined as a state that retains certain key properties when the system moves along the reaction coordinate [2]. For example, the generalized Mulliken-Hush scheme, a useful method for for electron transfer, retains the dipole moment in the diabatic states [3]. The fragment excitation difference scheme is a similar method for energy transfer problems, in which the excitation population is localized to each fragment [4].

The electronic coupling for singlet fission, an important parameter for determining the rate, has been found to be too small unless charge-transfer (CT) components were introduced in the diabatic states, mostly through perturbation or a model Hamilto- nian. In the present work, the Fragment Spin Difference (FSD) scheme was generalized to calculate the singlet fission coupling. The largest coupling strength obtained was 14.8 meV for two pentacenes in a crystal structure, or 33.7 meV for a transition-state structure, which yielded singlet fission lifetime of 239 or 37 fs, generally consistent to experimental result (80 fs). Test results with other polyacene molecules are similar. We found that the charge on one fragment in the S1 diabatic state correlates well with FSD coupling, indicating the importance of the CT component. The FSD approach is a useful first-principle method for singlet fission coupling, without the need to include the CT component explicitly [5].

References

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