Our Recent Studies on Vibronic Coupling: Applications in Singlet Fission and Paper-and-Pencil Works on Deriving Hamiltonians

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Singlet fission (SF) converts one short-lived singlet exciton to two long-lived triplet excitons, and can potentially enhance the photoelectric conversion efficiency in organic photovoltaic devices. In the new concept of intramolecular singlet fission (iSF), two chromophore units are covalently bonded and it is easier to adjust intermolecular morphology to facilitate SF. However, the detailed iSF mechanism is still unknown. SF is a vibronic coupling problem, because the conversion from the bright single-excitonic state to the dark multi-excitonic state is a nonadiabatic process. We used our recently coded diabatization scheme[1] to construct vibronic models for two iSF problems, one with the chromophore units in direct contact and the other with the chromophore units being connected by a covalent linker.[2,3] Through performing quantum chemistry calculations and quantum dynamics simulations, we investigated the general small size effects in iSF and presented a step-by-step picture for the through-linker iSF. With the new understanding, we propose a strategy to enhance the iSF efficiency by making appropriate substitution on the linker. In addition to these application studies of vibronic coupling, we are also interested in purely theoretical development. We focus on deriving general formalism of Jahn-Teller and pseudo-Jahn-Teller problems. More and more studies reveal that traditional second order expansions of the JT and pJT vibronic Hamiltonians in vibrational coordinates are inadequate. Our derivations for the general expansion formulas up to arbitrary order for trigonal, tetrahedral, and octahedral systems[4,5] will be presented.

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[1] T. Zeng, *J. Chem. Phys.* **2017**, *146*, 144103.
[2] T. Zeng* and P. Goel, *J. Phys. Chem. Lett.* **2016**, *7*, 1351-1358.
[3] T. Zeng, *J. Phys. Chem. Lett.* **2016**, *7*, 4405-4412.
[4] T. Zeng* and I. Seidu, *Phys. Chem. Chem. Phys.* **2017**, *19*, 11098-11110.
[5] T. Zeng*, R. J. Hickman, A. Kadri, and I. Seidu, *J. Chem. Theory Comput.* **2017**, DOI: 10.1021/acs.jctc.7b00787