Theoretical Studies on Molecular Aggregates

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Keywords	Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates exhibit characteristic optical and electronic properties that are not observed in isolated molecules. For example, their photophysical processes include electronic energy transfer and charge separations, which are desirable for low-cost electronic devices.

We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave function can be delocalized by electronic couplings due to molecular interactions; it is modulated by molecular vibrations. It is thus essential to consider electronic couplings and electron–phonon couplings on the same footing. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. An electronic structure of an aggregate is described as tight-binding Hamiltonian with electronic couplings obtained from the fragment molecular orbital method. The energy or charge dynamics is described by quantum
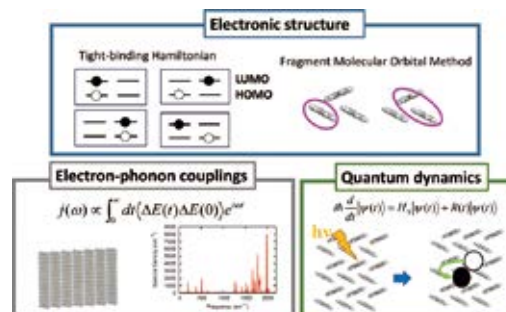

Figure 1. A combine approach to quantum dynamics in molecular aggregates.

dynamics methods with incorporating finite-temperature effects and electron–phonon couplings. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

We currently investigate electronic structures and exciton dynamics in organic optoelectronic materials, such as an organic/organic interface. We also develop an ab initio theory suitable to treat electronically excited states of large systems with reasonable accuracy, on the basis of a fragment-based approach and a many-body perturbation theory.

Selected Publications

• T. Fujita, J. C. Brookes, S. K. Saikin and A. Aspuru-Guzik, "Memory-Assisted Exciton Diffusion in the Chlorosome Light-Harvesting Antenna of Green Sulfur Bacteria," *J. Phys. Chem. Lett.* **3**, 2357–2361 (2012).

• T. Fujita, J. Huh, S. K. Saikin, J. C. Brookes and A. Aspuru-Guzik, "Theoretical Characterization of Excitation Energy Transfer in Chlorosome Light-Harvesting Antennae from Green Sulfur Bacteria," *Photosynth. Res.* **120**, 273–289 (2014).

1. Development of the Fragment Molecular Orbital Method for Calculating Non-Local Excitations in Large Molecular Systems[1]

Predicting electronically excited states of large molecular systems is still a challenging issue in quantum chemistry. In this study, we develop an excited-state theory suitable to treat large systems based on the fragment molecular orbital (FMO) method and the configuration interaction single theory with localized molecular orbitals. Although the FMO method have been well established for calculating local excited states, it is not straightforward to compute non-local excited states. We thus develop the theory which can compute non-local excitation of large molecular systems.

The method is based on the configuration interaction single (CIS) theory and was designed to reproduce low-energy excited states for a whole system with small dimensions. In order to describe non-local excited-states for the whole system, configuration state functions (CSFs) were constructed from localized MOs and the CIS amplitudes of intrafragment excitation via ground-state FMO and MLFMO-CIS calculations. The excited states of the whole system were written as the superposition of fragment CSFs for local excitations and interfragment charge transfer (CT) excitations. Exploiting fragment CSFs allows for efficient truncation of the dimension of the excited-state Hamiltonian. The excited-state Hamiltonian represented with fragment CSFs are calculated, and the resulting generalized eigenvalue problem is solved to determine the excited states of the whole system. The one-electron part of the excited-state Hamiltonian was treated by the FMO-linear combination of molecular orbital method, while the two-electron parts were efficiently treated within the two-body expansion of the FMO.

The theory was implemented based on the ABINIT-MP program package. The accuracy and efficiency of the present theory were tested for illustrative examples of molecular dimer and clusters. For example, the excitation energies of the face-to-face benzene dimer as a function of intermolecular distance is shown in Figure 2. FMO-CIS can reproduce the results of conventional CIS with quantitative accuracy for relatively large intermolecular distance of $R > 4$ Å. The mean absolute error relative to the conventional CIS is 26 meV at $R = 4$ Å. Regarding that the equilibrium distance of the face-to-face benzene dimer is $R = 3.8$ Å, the present theory can work with reasonable accuracy for practical applications. Similar benchmark calculations for π-stacked systems and realistic molecular crystals have confirmed that the absolute errors of 50 meV are achievable for molecular assemblies in their equilibrium geometries.

The present theory can compute a large number of excited states in large molecular systems; in addition, it allows for the systematic derivation of a model exciton Hamiltonian. These feature are useful for studying excited-state dynamics in condensed molecular systems based on the ab initio electronic structure theory.
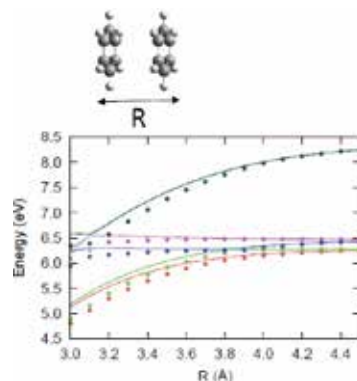

Figure 2. Excitation energies as a function of intermolecular distances from the conventional CIS (solid line) and the FMO-CIS (filled circles). The results shows energies of first six excited states.

2. Interfacial Charge Transfer States in the Pentacene/C$_{60}$ Interface

The electronic structures at organic–organic interfaces comprising electron–donor and electron–accepter materials are of great importance in the performance of various electronic devices. In organic photovoltaic (OPV) devices, interfacial charge-transfer states play critical roles in both charge separation and charge recombination processes. Despite their critical importance, it is difficult to experimentally investigate the interfacial CT states.

In this study, we consider an organic/organic interface that in composed of pentacene molecules as electron donor and C$_{60}$ molecules as electron acceptor. To characterize CT state manifold, we apply the FMO-based excited state theory to the pentacene/C$_{60}$ interface containing about 50 molecules. The structure was extracted from a bilayer interface modeled by a molecular dynamics simulation. The calculated energy (1.1 eV) of the lowest CT state is in reasonable agreement with the experimental reported value. We have analyzed CT states in terms of electron–hole (e–h) separation and delocalization of electron or hole wave function. We have found that in the energy region lower than pentacene absorption, CT states are localized with their small e–h separations, while CT states are delocalized with larger e–h separation in higher-energy region. In addition, the mixing among the interfacial CT states and pentacene excited states enhance the delocalization of electron wavefunction over the pentacene and C$_{60}$ molecules.

References

1) T. Fujita and Y. Mochizuki, submitted.
2) T. Fujita , Md. K. Alam and T. Hoshi, in preparation.