Theoretical Studies on Molecular Aggregates

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Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. 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. Our research also include the developments of theoretical and computational methods.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron-phonon or electron-vibration interaction. 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. Electronic states of an aggregate are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian
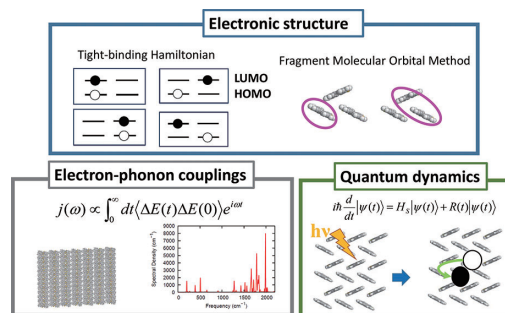
Figure 1. A combine approach to quantum dynamics in molecular aggregates.

is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron-vibration interactions. The combined computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the manybody perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

• T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, "Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2'3'-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization," *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).

• T. Fujita and Y. Mochizuki, "Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems," *J. Phys. Chem. A* **122**, 3886–3898 (2018).

## 1. Development of FMO-Based Exciton Model within GW/BSE[1]

Organic optoelectronic devices based on π-conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the electronically excited states is essential for understanding the optoelectronic processes governing the device operation and for rationally designing novel materials. However, accurate calculations of electronic states of organic materials which contain a lot of organic molecules or polymers are still challenging task. Successful theoretical descriptions require an accurate quantum mechanical method. In addition, the effects of polarizable environment must be appropriately taken into account.

In this study, we present the large-scale GW/Bethe-Salpeter equation (BSE) method that enables the computations of delocalized excited states in large molecular assemblies. The many-body Green's function method within the GW approximation can offer practical schemes to calculate electronic states within reasonable accuracy. However, the applications of GW and GW/BSE to large systems were difficult because of their considerable computational times. Here, we develop large-scale GW/BSE method for large systems based on the fragment molecular orbital methods. We have proposed the fragmentation approximations of total polarization functions and ΔCOHSEX approximation that neglects the dynamical polarization of surrounding fragments. We have confirmed that the FMO-GW/BSE method enables accurate calculations of localized electronic states in large systems. Furthermore, the FMO-GW/BSE method was combined with the exciton model to calculate delocalized excited states in molecular aggregates. In the exciton model, the excited-state Hamiltonian for an entire system is calculated in the diabatic basis and then diagonalized to approximate the adiabatic excited states. The FMO-based exciton model utilizes the fragment configuration state functions (CSFs) for intrafragment excited states and for interfragment charge-transfer states, and the excited-state Hamiltonian at the GW/BSE level is calculated in the basis of fragment CSFs. We have shown that the results of unfragmented calculations can be reasonably reproduced; thus, the present FMO-GW/BSE method can offer efficient and practical schemes for investigating realistic molecular aggregates.

2. Revisiting the Electronic Structure of PEN/C_{60} Bilayer Heterojunctions[2]

Molecular orientations and interfacial morphologies have critical effects on the electronic states of donor/acceptor interfaces and thus on the performance of organic photovoltaic devices. Here, we investigate the charge-transfer (CT) states in pentacene(PEN)/C_{60} interfaces as model systems and highlight the polarization and delocalization effects. The effects of polarization and delocalization on the interfacial CT states are

schematically represented in Figure 2. In a gas phase (Figure 2 (a)), the energy of the CT state is given by the highest-occupied molecular orbital (HOMO) energy of a donor molecule, the lowest-unoccupied molecular orbital (LUMO) energy of an acceptor molecule, and the Coulomb interaction between the electron and the hole. The solid-state polarization effects reduce the energy gap between the donor HOMO and the acceptor LUMO (Figure 2 (b)) and weakens the e–h interaction. In a solid phase, the electron or hole wave function can be delocalized over multiple acceptor or donor molecules, and delocalized CT states can be formed (Figure 2 (c)). This charge delocalization can further shift the energy gap and
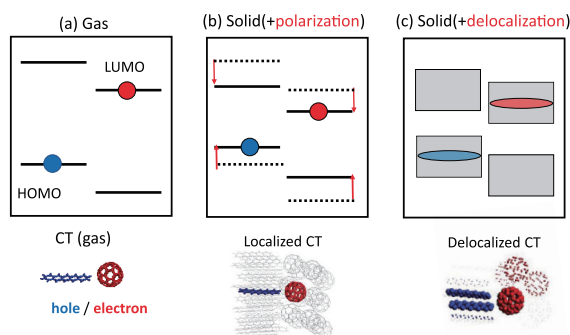
Figure 2. Schematics of solid-state effects on the interfacial charge-transfer states.

possibly weaken the e–h interaction.

In this study, we explore the energy levels and CT states at the organic donor/acceptor interfaces on the basis of the fragment-based GW/BSE approach. The face-on and edge-on orientations of pentacene/C_{60} bilayer heterojunctions have employed as model systems. The FMO-GW/BSE calculations were performed for the local interface structures in the face-on and edge-on bilayer heterojunctions, which contain approximately 2,000 atoms. Calculated energy levels and CT state absorption spectra are in reasonable agreements with those obtained from experimental measurements. We found that the dependence of the energy levels on interfacial morphology is predominantly determined by the electrostatic contribution of polarization energy, while the effects of induction contribution in the edge-on interface are similar to those in the face-on. Moreover, the delocalized CT states contribute to the main absorption peak in the edge-on interface, while the face-on interface features relatively localized CT states in the main absorption peak. The impact of the interfacial morphologies on the polarization and charge delocalization effects is analyzed in detail.

References

1) T. Fujita and Y. Noguchi, in preparation.
2) T. Fujita, Y. Noguchi and T. Hoshi, *Materials* **13**, 2728 (2020).