

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 includes 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 is used for simulating energy or charge dynamics by a quantum

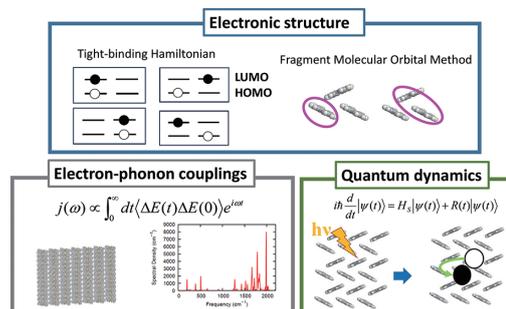


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

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 many-body 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'-]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. Fragment-Based Excited-State Calculations Using the GW Approximation and Bethe–Salpeter Equation¹⁾

Accurate calculations of electronic states are essential for the computational studies of organic semiconductor materials, toward understanding of electronic processes in organic devices. The electronic processes in organic electronic devices, such as charge injection and electron–hole separation, are governed by the energies of the charged and neutral excited states. Although the Kohn–Sham (KS) density functional theory (DFT) has been established to be accurate for investigating the ground-state properties, a more sophisticated method is required for excited states. The many-body Green’s function method within the GW approximation has been established as a standard approach for the first-principle computation of the charged excitations in condensed matter. Further, neutral excited states can be computed using the Bethe–Salpeter equation (BSE) within the GW approximation, *i.e.*, the GW/BSE method. In particular, the GW/BSE method can yield the correct long-range asymptotic behaviors of the charge-transfer excited states in both gas and condensed phases, which is in contrast to the standard time-dependent DFT.

In this study, we present a fragment-based approach for calculating the charged and neutral excited states in molecular systems, based on the many-body Green’s function method within the GW approximation and Bethe–Salpeter equation. Our implementation relies on the many-body expansion of the total irreducible polarizability in the basis of fragment molecular orbitals. The GW quasiparticle energies in complex molecular environments are obtained by the GW calculation for the target fragment plus induced polarization contributions of the surrounding fragments at the static Coulomb-hole plus screened exchange level. In addition, we develop a large-scale GW/BSE method for calculating the delocalized excited states of molecular aggregates, based on the fragment molecular orbital method and the exciton model. The accuracy of fragment-based GW and GW/BSE methods were evaluated on the molecular clusters and molecular crystal. We found that the accuracy of the total irreducible polarizability can be improved systematically by including two-body correction terms, and the fragment-based calculations can reasonably reproduce the results of the corresponding unfragmented calculations with a relative error of less than 100 meV. The proposed approach enables the efficient excited-state calculations for large molecular systems with reasonable accuracy.

2. Excited-State Dynamics Based on the FMO and Wavepacket Propagation Method²⁾

We develop a method to investigate the excited-state dynamics in organic molecular aggregates. Our approach is based on three components: (i) FMO-based electronic coupling calculations, (ii) derivations of model Hamiltonians, and (iii) a wavepacket dynamics method. Using the electronic couplings obtained from an FMO calculation for an aggregate, we derive a model Hamiltonian that describes a charge carrier or an exciton in the aggregate. From a theoretical viewpoint, an *ab initio* many-electron Hamiltonian can be mapped into a reduced one-body or two-body Hamiltonian through the FMO calculation. The time evolution of the model Hamiltonian is then simulated using a wavepacket propagation method. We attempt to understand photophysical and optoelectronic processes in a molecular aggregate as the quasiparticle dynamics described by the model Hamiltonian. We have implemented the electronic coupling calculations and model Hamiltonian derivations into the ABINIT-MP program. In view of computations, an FMO calculation by the ABINIT-MP program provides Hamiltonian matrix elements. The matrix data are then passed to other software that simulates the time propagation.

We investigated the excited-state dynamics in the DNTT thin film and the C₆₀/pentacene (PEN) interface. In particular, we highlight the spatial extents of the electron and hole wave functions that constitute exciton states. We show that the dynamics of the electron and hole wave functions play essential roles in optoelectronic processes, such as the exciton relaxation dynamics and charge separation. Because the extent of delocalization is determined by the interplay among electronic couplings, structural disorder, and finite-temperature effects, the combined approach based on the FMO and wavepacket dynamics is indispensable. Although we have focused on the organic materials, our approach is general and can be applied to other molecular systems. Potential applications include functional supramolecular systems and bio-inspired materials, as well as organic electronic materials.

References

- 1) T. Fujita and Y. Noguchi, submitted.
- 2) T. Fujita and T. Hoshi, *Recent Advances of the Fragment Molecular Orbital Method*, Y. Mochizuki, S. Tanaka and K. Fukuzawa, Eds., Springer; Singapore, pp. 547–566. (2021).