

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, and 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 is obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian

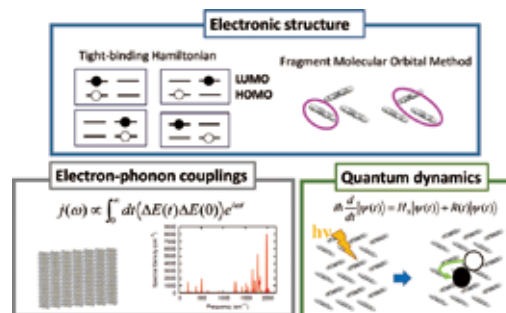


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron-vibration interactions. The combine 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'-*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 Large-Scale GW Method for Applications to Organic Optoelectronic Materials¹⁾

Organic electronics based on π -conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the charged-transport levels or optical excitations is essential for understanding the electronic processes governing the device operation and for rationally designing novel materials. The successful theoretical descriptions of charged and neutral excited states require an accurate quantum mechanical method: In addition, the effects of polarizable environment must be appropriately taken into account. For example, an electron addition or removal of a molecule induces the polarization of the surrounding molecules, which results in the reduction of HOMO–LUMO gap. The polarization induced by the neutral excitation (creation of electron–hole pair) increases with increasing the electron–hole separation, leading to the relative stabilization of the charge-separated states. Note that such the environmental polarization is state-specific and cannot be treated by a standard electrostatic embedding scheme.

Here, we present a method that can treat both the electron correlation and the state-specific polarization, on the basis of the fragment molecular orbital and GW methods. The GW is a many-body Green's function theory and can offer an accurate and practical scheme to calculate a quasiparticle energy corresponding to an ionization potential or an electron affinity. Electronically excited states can be also computed in combination with Bethe-Salpeter equation method. In this study, we develop the large-scale GW method based on the FMO method. The implementation is based on the fragmentation approximation of the polarization function and the combined GW and Coulomb-hole plus screened exchange approximations for self-energies. As well as the ground-state polarization treated in the FMO method, the FMO-GW method can describe the state-specific polarization effect.

The fragment-based GW was demonstrated in application to the charge-transfer states formed across the pentacene (PEN)/C₆₀ bilayer heterojunction. The local interface structure approximately contains 2,000 atoms, with external molecules in the total bilayer heterojunction structure being treated by external point charges. The CT excitation energies were estimated from the quasiparticle energies and electron–hole screened Coulomb interactions and are in reasonable agree-

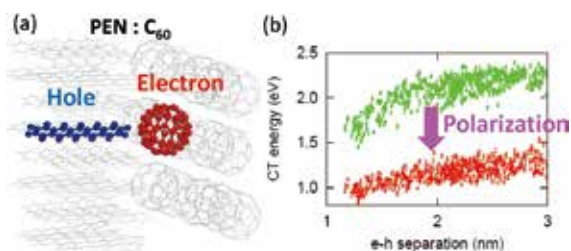


Figure 2. (a) The atomic structure of pentacene/C₆₀ local interface. (b) The CT excitation energy with respect to electron–hole separation.

ment with experimental estimates from the external quantum efficiency measurements. We highlight the impact of the induced polarization effects on the electron–hole energetics.

2. Polarization Energy of Pentacene Clusters²⁾

We investigate the electronic states of PEN clusters. The electronic states of PEN have been studied by calculations for an isolated molecule or molecular crystals. Although an isolated PEN molecule and PEN crystals have been well studied, the evolution of electronic states from the gas to the solid phase still remains unclear. In this study, we employ PEN clusters, (PEN)_N ($N = 3, 14, 33$), as model systems and consider the effects of molecular packing and intermolecular interactions on the electronic states. Figure 3(b) show the HOMO–LUMO gap and S1 excitation energy of a PEN molecule in the central region in the cluster structures. The HOMO–LUMO gap and S1 excitation energy of an isolated PEN molecule are 4.83 and 2.08 eV, respectively, at the GW@B3LYP/6-31G* level. The HOMO–LUMO gap decreases with increasing the cluster size. For the intramolecular excited states, the reduction of the HOMO–LUMO gap is compensated by the weakening of the electron–hole attraction, leaving the excitation energy unchanged.

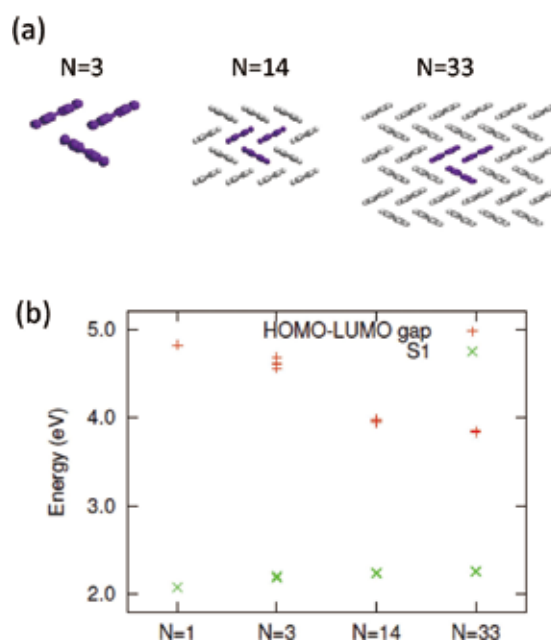


Figure 3. (a) The structures of PEN clusters. (b) The HOMO–LUMO gap and S1 excitation energy of a pentacene molecule in the central regions in cluster structures.

References

- 1) T. Fujita, Y. Noguchi and T. Hoshi, *J. Chem. Phys.*, accepted.
- 2) T. Fujita, in preparation.