

Theoretical Studies on Molecular Aggregates

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Professional Employment

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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

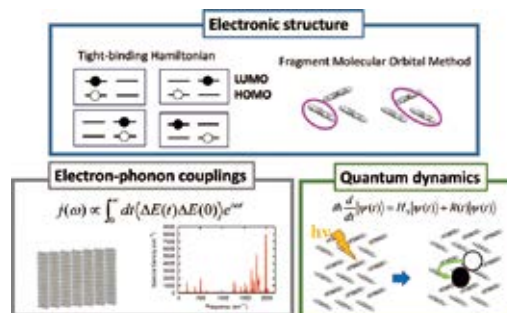


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

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'-]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. Interfacial Charge-Transfer States at Organic Bilayer Heterojunction¹⁾

The electronic structures at organic–organic interfaces comprising electron-donor and electron-accepter materials are of great importance in the performance of the organic solar cells. In particular, the interfacial charge-transfer (ICT) state—an electron-hole pair formed across the donor/acceptor interface—plays an essential role in charge photogeneration because it is an intermediate for both charge separation and charge recombination processes. Despite their critical importance, it is difficult to experimentally investigate the interfacial CT states.

Here, we performed *ab initio* excited-state calculations to investigate the ICT states formed at a pentacene/C₆₀ bilayer heterojunction modeled by molecular dynamics simulations. The model bilayer heterojunction structures contain approximately 1.8×10^5 atoms, and their local interface regions containing 2,000 atoms were treated quantum mechanically, embedded in the electrostatic potentials from remaining parts. Therefore, the charge delocalization effect, structural disorder, and the resulting heterogeneous electrostatic and polarizable environments were taken into account in the excited-state calculations. The computed energies of the low-lying ICT states are in reasonable agreement with experimental estimates. By comparing the edge-on and face-on configurations of the pentacene/C₆₀ interfaces, we highlight the influence of interfacial morphologies on the energetics and charge delocalization of ICT states. We found that, in the edge-on configuration, the pentacene absorption region is resonant with dense delocalized ICT states, resulting in the formation of hybridized states. The hybridization enhances the delocalization of ICT states, owing to their electron wave functions extending across the pentacene/C₆₀ interface. In addition, the delocalized ICT state can be directly accessed by photoexcitation, borrowing absorption intensity from pentacene excited states. Such the optically-bright delocalized ICT states enable photoinduced long-range electron transfer through the extended electron wave functions, giving rise to rapid charge separations.

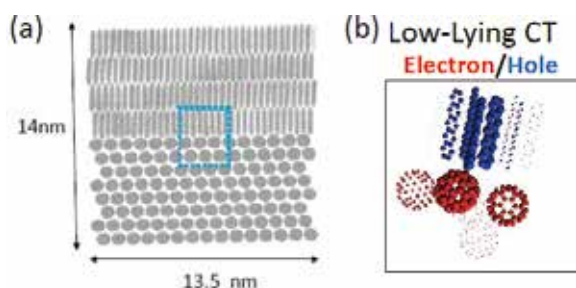


Figure 2. (a) The atomic structure of pentacene/C₆₀ bilayer heterojunction. (b) Visualization of electron (red) and hole (blue) wave functions that constitute the low-lying CT state.

2. Development of Many-Body Green's Function Method for Large Molecular Systems²⁾

The GW many-body Green's function approach has been established as an accurate and efficient method to predict the electronic levels. Within the GW method, the dielectric function is computed for screened Coulomb interaction, and the self-energy is approximated from the Green's function and the screened Coulomb potential. The GW method can be combined with the Bethe-Salpeter equation to obtain electronically excited states. The GW/BSE method have been applied to isolated molecules or periodic systems. However, they were not applied to interface systems because large and disordered system must be treated.

We develop the fragment-based GW method suitable to treat large molecular systems in heterogeneous polarizable environments, on the basis of the fragment molecular orbital (FMO) method. The Green's function of a total system is approximated from fragment Green's functions that are calculated by fragment molecular orbitals and is expanded up to two-body terms. The screened Coulomb potential is approximated from the sum of intrafragment density-response functions, with interfragment polarization terms being neglected. The approximations of the Green's function and screened Coulomb potential lead to the many-body expansion of the self-energy; this expansion is essentially equivalent to the many-body expansion of the Fock matrix in the FMO method. To deal with large molecular systems, the present implementation relies on the Coulomb hole plus screened exchange (COHSEX) approximation, which is the static limit of GW. The accuracy of the FMO-COHSEX method is demonstrated in comparison to conventional COHSEX results for organic molecular aggregates. We confirmed that the present fragmentation approach can provide resonantly accurate results, and the mean absolute errors of quasiparticle energies less than 0.1 eV have been achieved for valence orbitals. We also investigate the accuracy of the COHSEX approximation for describing the effects of molecular aggregation of electronic states, by comparing them to the GW method. Although the COHSEX fails to quantitatively determine quasiparticle energies, it was found to successfully describe the molecular aggregation effects on electronic states, such as induced polarization and dispersion effects. As an illustrative application of the present method, we consider the electronic states of the pentacene thin film. We discuss the impact of induced polarization effect in the heterogeneous environment, highlighting the gap renormalization and the polarization-induced localization. The application shows that our fragment-based GW method is useful to study electronic structures of molecular aggregates in complex environments.

References

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