Quantum dynamics of electron transfer in strongly coupled environments

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Experiments of time-resolved bidimensional spectroscopy carried out in complex systems, such as photosynthetic systems (FMO)[1] or conjugated polymers[2], showed that quantum coherences amongst electronic excited states can persist for long times, comparable to the electron or excitation energy transfer times.

In order to investigate these phenomena from a theoretical point of view, one needs to study the quantum motion of the nuclei and its influence onto the transfer. In the systems at stake, photo-induced electron transfer are studied in an oligothiophene-fullerene heterojunction[3] and a chromoprotein cryptochrome[4] as shown on Fig. 1 with a realistic environment.
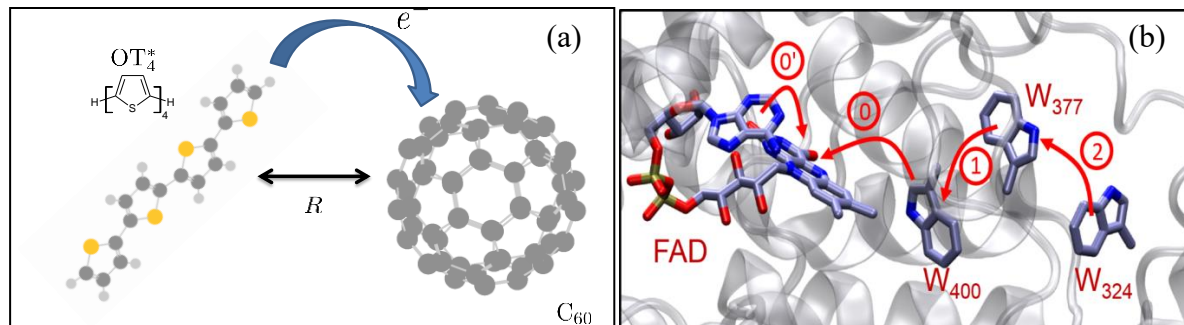

Figure 1 Photo-induced electron transfer systems under study: On the left (Panel (a)), oligothiophene (OT$_4$) – fullerene (C$_{60}$) heterojunction. On the right (Panel (b)), chromoprotein cryptochrome with a flavin-adenosin-diphosphate (FAD) chromophore and a chain of three tryptophan molecules (W$_{400}$, W$_{377}$ and W$_{324}$)

For the heterojunction (Fig. 1 (a)), a reference Hamiltonian[5] describing a donor-acceptor electronic system coupled to a bath of harmonic oscillators has been used. For the cryptochrome (Fig. 1 (b)), a three electronic states Hamiltonian has been parameterized using QM/MM trajectories based on constrained DFT (cDFT).[6,7]

Based on these parametrized Hamiltonians, time propagations have been carried out using methods of dissipative quantum dynamics. However, since these systems exhibit a strong system-bath coupling that cannot be handled with traditional perturbation theory, one has to resort to exact computations such as the hierarchical equation of motion method.[8] A special care has also been taken to evaluate the quantum memory effects which prove to be significant in these systems.[9] To catch a glimpse of the physical movement at stake in the transfer, we perform a coordinate transformation used to define an effective mode[10], which is included into the system, and which itself is coupled to a secondary bath.

As main results, we show and explain the dynamical behavior of various cases leading to an easy delocalization or to a trapping of the charge and assess the time scales of the transfer.

In the cases considered, the proposed methodology is well suited to analyze the subtle interplay between charge transfer and nuclear deformations, a prototype situation for many important processes in chemical and biological systems.

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