

# Dynamics of open quantum systems: Electron transfer in mixed-valence compounds

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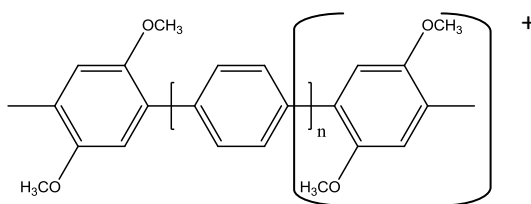
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Experiments of time-resolved bidimensional spectroscopy carried out in complex systems, such as photosynthetic systems (FMO) [1] or conjugated polymers [2], showed that quantum coherences amongst electronic excited states can persist for long times, 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. The systems under study are mixed-valence organic compounds from which experimental data have been published [3]: aromatic polymers (as shown on the following figure) exhibiting donor-acceptor sites (1,4-dimethoxy-3-methylphenylene) bound by an increasing chain of n-paraphenylenes rings.



To this end, a Hamiltonian describing a donor-acceptor electronic system coupled to a bath of harmonic oscillators has been parameterized using the new method of constrained DFT (cDFT) [4]. In order to treat the bath perturbatively, a coordinate transformation is used to define a reaction path, which is included into the system, and which itself is coupled to a secondary bath [5,6]. According to the bridge length, we can examine different situations leading to a ground adiabatic state with or without barrier.

Then, time propagations have been carried out using methods of dissipative quantum dynamics, based on a Markovian perturbative master equation approach [7,8] at different temperatures. 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. We believe that the proposed methodology, applied to model systems in this work, might be 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.

[1] G. S. Engel et al, *Nature*, **446**, 78 (2007)

[2] E. Collini and G. Scholes, *Science*, **323**, 369 (2009)

[3] S.V. Lindeman, S. V. Rosokha, D. Sun and J. K. Kochi, *J. Am. Chem. Soc.*, **124**, 5, 843 -855 (2002)

[4] Q. Wu, T. Van Voorhis, *J. Chem. Theory Comput.*, **2**,765-774 (2006)

[5] A. Pereverzev, E. R. Bittner, I. Burghardt, *J. Chem. Phys.*, **131**, 034104 (1999)

[6] A. Chenel, E. Mangaud, I. Burghardt, C. Meier, M. Desouter-Lecomte, *J. Chem. Phys.*, **140**, 044104 (2014)

[7] A.G. Redfield, *Adv. Magn. Reson.*, **1**, 1 (1965)

[8] W.T. Pollard, A. K. Felts, R. A. Friesner, *Adv. Chem. Phys.*, **63**, 77-134 (1996)